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THE CRYSTALLINE APPEARANCE OF CALCIUM TARTRATE AS A DISTINCTIVE AND DELICATE TEST FOR THE PRESENCE OF TARTARIC ACID OR TARTRATES.

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The necessity of ascertaining the presence of tartaric acid in connection with the study of the composition of various fruit syrups, ciders, compound wines, baking powders, etc., makes desirable a reliable method for its detection.

A method is described below which has given very satisfactory results, proving, on the whole, more reliable than the identification by means of the precipitation of the acid potassium tartrate, or by the silver nitrate reduction test.

Use is made of the familiar reaction of tartrates with calcium chloride. Soluble tartrates, when treated with calcium chloride, give a precipitate of calcium tartrate which becomes crystalline on standing, the precipitate forming in dilute solutions only after some hours.

With the aid of the microscope the above reaction furnishes the basis for a delicate test for tartaric acid in various substances.

By experiment it was found that when a solution containing tartaric acid in small amount, was treated as described below, crystals of calcium tartrate, in the form of rhombic prisms or pyramids, separated out. These crystals are readily recognized under a low power microscope, magnification 75 to 100 diameters, and are characteristic of tartaric acid.

Preparation of Solution.

(1) The solution to be tested should be concentrated to a small bulk. In the case of fruit juices, wine and ciders, when the amount of tartaric acid is thought to be very small, 150–200 cc. may be evaporated to 50 cc. The solution, after concentration, should not contain more than 30 per cent of solid matter, sugar, dextrin, glycerin, etc.

(2) In the case of fruit syrups of high content of solids, it is advisable to precipitate the organic acids with lead subacetate, and after decomposing the precipitate with hydrogen sulphide, to make use of the concentrated solution containing the acids.

Method of Procedure.

The solution of about 50 cc. prepared by (1) or (2), according to the nature of the sample, is cooled and made slightly alkaline with potassium hydroxide, a few drops of potassium acetate, 20 per cent solution, is added and, after acidifying with acetic acid, about 10 cc. of calcium chloride, 30–40 per cent solution, added, and the whole stirred rapidly for a minute or two. After standing at room temperature for 12–15 hours, the solution may be decanted off and the crystals of calcium tartrate, if present, will be seen in the bottom of the beaker. These, under the microscope, appear as characteristic prisms, similar to those in Plate I. The crystals vary a great deal in size, according to the amount of tartaric acid present in the solution.

As a rule, when only a small amount is present, the crystals are approximately the size of those shown in Plate I. When

sufficient tartaric acid is present so as to be precipitated within an hour or two, the crystals resemble in size and shape those in Plate II. Isolated prisms of a smaller size, but of identical shape as those in Plate I., will be readily observed.

In the examination of compound ciders and fruit juices, if tartaric acid is present in sufficient quantity to give a crystalline precipitate in a few minutes, and the crystals are not characteristic, it is advisable to make a new test, using less of the sample. Crystallization from a dilute solution gives more characteristic crystals, as noted above.

Tartaric Acid in Succinic Acid.

Five per cent of tartaric acid in succinic acid may be readily detected.

Two grams of succinic acid should be dissolved in 40 cc. of of water, and after neutralizing with potassium hydroxide, a few drops of potassium acetate are added, then 10 cc. calcium chloride solution and 3 cc. glacial acetic acid.

Tartaric acid, if present in quantity equal to 5 per cent, will give crystals of calcium tartrate similar to those in Plate I., after standing for several hours.

Study was made of the following substances: Tartaric acid, wine, citric, malic, succinic, oxalic and aconitic acids.

The effect of the addition of mineral acids was also noted.

Experiments with Wine.

Several tests of the method were made with different wines, containing varying amounts of tartaric acid.

Characteristic crystals of calcium tartrate were obtained with wine diluted to 50 cc. and containing as low as 0.05 gram of total tartaric acid. A wine containing 39 per cent of solids, consisting of the natural solids and added sugar and glycerin, and 0.0625 gram of total tartrates in 50 cc. of solution, gave positive results.

Tartaric Acid—The following tests were made with tartaric acid:

Tartaric acid.	Volume of solution.	Remarks.
0.05 gram	50 cc. of water	Characteristic crystals of calcium tartrate
0.05 gram	50 cc. (25 per cent solids, sugar and glycerin)	Characteristic crystals of calcium tartrate
0.05 gram	50 cc. (10 per cent solids, cane sugar)	Characteristic crystals of calcium tartrate
0.05 gram	50 cc. (35 per cent solids, sugar)	Characteristic crystals of calcium tartrate
0.05 gram	50 cc. (26 per cent solids, equal parts of glycerin and sugar)	Characteristic crystals of calcium tartrate
0.1 gram	50 cc. (50 per cent sugar solution)	Characteristic crystals of calcium tartrate
0.1 gram	50 cc. (50 per cent glycerin solution)	Characteristic crystals of calcium tartrate
0.1 gram	50 cc. (45 per cent solids, 25 per cent sugar and 20 per cent glycerin)	Characteristic crystals of calcium tartrate

Oxalic Acid.—Oxalic acid gives a precipitate of calcium oxalate with calcium chloride, but this precipitate does not resemble the calcium tartrate. When tartaric acid is present with the oxalic acid, crystals of calcium tartrate will be found floating on the top of the solution. These may be gathered on a stirring rod, placed on a slide and examined under the microscope.

Tartaric and oxalic acids.	Volume of solution.	Remarks.
0.1 gram tartaric acid + 1.0 gram oxalic acid	50 cc. of water	Crystals of calcium tartrate present
0.05 gram tartaric acid + 0.5 gram oxalic acid	50 cc. of water	Crystals of calcium tartrate present

Succinic Acid.—Tests were made with succinic acid, as follows:

Succinic acid.	Volume of solution.	Remarks.
1 gram succinic acid	50 cc.	No precipitate
1 gram succinic acid + 0.05 gram tartaric acid	50 cc.	Crystals of calcium tartrate obtained
2 grams succinic acid + 1 gram tartaric acid	50 cc.	Crystals of calcium tartrate obtained

In these tests with succinic acid 3 cc. of acetic acid were added to the solution after the addition of the calcium chloride.

Citric acid.	Volume of solution.	Remarks.
1 gram citric acid	50 cc.	Heavy precipitate of calcium citrate. Acetic acid was added to similar solutions, in amount varying from 1 to 5 cc., but beyond making the precipitate in the form of a crust, there was no other effect
0.5 gram citric acid 0.1 gram tartaric acid	50 cc.	Heavy precipitate of calcium citrate. A few crystals of calcium tartrate were observed after standing for 2 hours
0.1 gram citric acid 0.1 gram tartaric acid	50 cc.	Heavy precipitate of calcium citrate. A few crystals of calcium tartrate were observed after standing for 2 hours
0.1 gram citric acid + 0.05 gram tartaric acid	50 cc.	Precipitate of calcium citrate, test negative

Owing to the precipitation of calcium citrate when citric acid is present in greater quantity than tartaric acid, the form of the calcium tartrate crystals is changed and the test is liable to fail. If the precipitate, or some of the crystals obtained, are dissolved in a small amount of nitric acid and the calcium precipitated with sodium carbonate, the filtrate containing the tartaric and citric acids will give a silver mirror with the silver nitrate reduction test. Neither malic, citric, nor succinic acids reduce the silver nitrate and form a mirror.

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Malic Acid.—

Malic acid.	Volume of solution.	Remarks.
1 gram malic acid	50 cc. water	No precipitate
1 gram malic acid + 0.05 gram tartaric acid	50 cc. water	Plates and needles. Calcium tartrate crystals are not characteristic as in Plate I.
0.5 gram malic acid + 0.1 gram tartaric acid	50 cc.	Plates and needles. Calcium tartrate crystals are not characteristic as in Plate I.

Malic acid gives no precipitate with calcium chloride. If it be present with tartaric acid it modifies the form of the calcium tartrate crystals. One having had considerable experience with the method would recognize the trouble, but it is safer to confirm the test by means of the silver nitrate reduction test, as described under citric acid.

Aconitic acid.	Volume of solution.	Remarks.
0.5 gram aconitic acid 0.1 gram tartaric acid	50 cc.	Characteristic crystals of calcium tartrate, although rather small in size
0.25 gram aconitic acid 0.1 gram tartaric acid	50 cc.	Characteristic crystals of calcium tartrate, although rather small in size

Tartaric and sulphuric acids.	Volume of solution.	Remarks.
0.1 gram tartaric acid 0.1 gram sulphuric acid	50 cc.	Crystals of calcium tartrate obtained
0.1 gram tartaric acid 0.25 cc. conc. sulphuric acid	50 cc.	Crystals of calcium tartrate obtained
2 grams tartaric acid 0.5 cc. conc. sulphuric acid	50 cc.	Crystals of calcium tartrate obtained
2 grams tartaric acid 1 cc. conc. sulphuric acid	50 cc.	Result doubtful

Alum and tartaric acid.	Volume of solution.	Remarks.
0.1 gram alum 0.5 gram tartaric acid	50 cc.	Negative
0.1 gram alum 0.1 gram tartaric acid	50 cc.	Negative

Mixtures.	Volume of solution.	Remarks.
0.5 gram citric acid 0.5 gram succinic acid 0.1 gram tartaric acid	50 cc.	Precipitate of feathery tufts with a few large crystals of calcium tartrate
0.5 gram citric acid 0.3 gram malic acid 0.1 gram tartaric acid	50 cc.	A precipitate of plates. Negative test. Presence of tartaric acid confirmed by the silver nitrate reduction test
0.1 gram malic acid 0.1 gram citric acid 0.1 gram succinic acid 0.075 gram tartaric acid	50 cc.	Crystals of calcium tartrate
0.5 gram malic acid 0.5 gram succinic acid 0.05 gram tartaric acid	50 cc.	Negative. Presence of tartaric acid confirmed by silver nitrate reduction test
0.05 gram tartaric acid 0.05 gram potassium sulphate	50 cc.	Crystals of calcium tartrate
0.1 gram tartaric acid 1.5 grams potassium chloride	50 cc.	Crystals of calcium tartrate

Conclusion.

The calcium tartrate crystals obtained by the method described above are characteristic for tartaric acid. None of the other organic acids gave crystals of a similar form with calcium chloride. When crystals, as shown in Plate I. or II., are obtained, positive conclusion is warranted that tartaric acid is present.

Citric and oxalic acids give a precipitate with calcium chloride; malic acid does not, but if present with tartaric acid, the form of the calcium tartrate crystals is changed, the crystals being in the form of plates and needles. It is believed that the mixtures containing tartaric and other acids which failed to give satisfactory tests with the method represented extreme cases, and that under ordinary conditions the method is reliable. The precipitation of tartaric acid as the bitartrate proved even more liable to failure than the precipitation as calcium tartrate.

In cases where a precipitate is obtained with calcium chloride, and no characteristic crystals of calcium tartrate can be observed, the presence or absence of tartaric acid may be proved, as follows:

Wash the precipitate with 50 per cent alcohol and dissolve in a small amount of nitric acid. Precipitate the calcium with sodium carbonate, to the filtrate add ammonia and a crystal of silver nitrate and heat in a test tube. A silver mirror will be obtained if tartaric acid is present.

The presence of alum, or of an excess of mineral acids interferes with the test, preventing the precipitation of calcium tartrate.

From a large number of experiments with the test, conclusion is warranted that it is a convenient and reliable method for detecting tartaric acid in wines, ciders, fruit syrups, etc., and it is believed to be possible to adapt it to other substances as occasion may arise.

THE RELATIVE MIGRATION VELOCITIES OF THE IONS OF SILVER NITRATE IN WATER, METHYL ALCOHOL, ETHYL ALCOHOL AND ACETONE, AND IN BINARY MIXTURES OF THESE SOLVENTS, TOGETHER WITH THE CONDUCTIVITY OF SUCH SOLUTIONS.

By Harry C. Jones and Charles A. Rouiller.

PART I.

HISTORICAL SKETCH.

1. Earlier Observations.

Shortly after solutions began to be subjected to the action of the current from the voltaic pile, it was noticed that changes were produced at the poles. Carlisle[1] observed that in the de composition of water alkali was formed at the cathode. This was later proved by Davy[2] to be due to the presence of saline impurities in the water. In the meantime it had been shown that this decomposition of salts, and the transference of the base to the negative pole and the acid to the positive electrode, was general, and Berzelius and Hissinger[3] proposed their famous electrochemical theory.

About 30 years later Faraday[4] performed some experiments to show that the passage of a current through a solution produces changes in concentration about the poles. Gmelin[5] observed that when a solution of copper sulphate is electrolyzed between copper electrodes, it becomes colorless at the cathode, while the blue color about the anode increases in intensity. Pouillet[6] found a similar change in concentration in a gold chloride solution.

In 1844 Daniel and Miller,[7] continuing the earlier experi-

[1] Nicholson: Gilbert's Ann., 6, 340 (1800). Ostwald: "Elektrochemie," p. 130.
[2] Phil. Trans., 1807, p. 1. Ostwald's "Klassiker," No. 45.
[3] Jour. d. Chem., 1, 115 (1803). Ostwald: "Elektrochemie," p. 317.
[4] Pogg. Ann., 32, 401 (1834).
[5] *Ibid.*, 44, 1 (1838).
[6] Compt. rend., 20, 1544 (1845).
[7] Phil. Trans., 1844, p. 1.

ments of Daniel,[1] made it clear that different ions do not travel with the same velocity. They electrolyzed solutions of various salts in a cell divided into compartments by porous membranes. Their experimental errors were so great, however, that they reached the erroneous conclusion that certain ions, such as those of copper and zinc, do not migrate at all.

Smee[2] performed many experiments which showed that the electric current causes changes in concentration, but he still advocated the Faraday theory of electrolysis.

2. Hittorf and His Method of Determining Transport Numbers.

The true explanation of these phenomena was finally offered by Hittorf,[3] in 1853. He showed that the changes in concentration about the poles were due to the fact that the anions and cations traveled with different velocities, and that the amount of the change was a measure of the relative velocities of the two ions. In this way he determined the transport numbers for a very large number of salts.[4] He devised various forms of apparatus, depending on the nature of the salt under investigation, but all were of the same general type —a vertical tube divided into sections by porous diaphragms. The cathode was placed in the upper and the anode in the lower cell.

Working with solutions of copper sulphate, he found that the current density and the temperature, between 4° and 21°, had no measurable effect on the transport number, but that the relative velocity of the copper ion increased with the dilution until it reached a constant, maximum value. Extending his investigations to other salts, he found that in some the transport number did not change with the dilution; others acted like copper sulphate, and in still others such as silver nitrate, the relative velocity of the cation decreased as the dilution increased.

The various forms of apparatus which he employed all have some objectionable features. The use of membranes, espe-

[1] Phil. Trans. 1839, p. 97; 1840, p. 209.
[2] Phil. Mag., **17**, 193 (1840); **25**, 434 (1844).
[3] Pogg. Ann., **89**, 177 (1853). Ostwald's "Klassiker," No. 21.
[4] Pogg. Ann., **89**, 1 (1856); **103**, 1 (1858); **106**, 337 (1859). Ostwald's "Klassiker," Nos. 21 and 23.

cially, may be a serious source of error. Hittorf[1] himself recognized this nearly 50 years later, and repeated many of his experiments, using silk web instead of animal membranes. He found that when solutions of alkali salts are forced by endosmose through porous diaphragms they are in no way changed, but solutions of the zinc and cadmium halides and many other electrolytes become more concentrated on the anode side, and the values obtained for the transport number of the cation are too low.

Hittorf's views met with extremely violent opposition, and for many years very little work was done in this field. Wiedemann,[2] in the course of his investigations on endosmose, measured the changes in concentration produced in various solutions by electrolysis. His apparatus consisted of two cylinders into which dipped glass tubes connected by rubber tubing.

Wieske[3] determined a few transport numbers in an apparatus made of two bottles of known volume, connected near the top by a lateral tube. To separate the solutions after electrolysis, this tube was provided with a glass stop-cock.

Burgoin[4] electrolyzed many organic acids and their salts, and studied quantitatively the products of decomposition. His apparatus consisted of two test-tubes, one inside the other, and communicating only by means of a small hole bored in the bottom of the smaller one.

Kirmis[5] modified the Wiedemann apparatus by substituting glass for the rubber connections.

About this time F. Kohlrausch,[6] as the result of a long series of conductivity measurements, was able to point out a close relationship between the velocities of ions and the conductivities of solutions. He showed that, in dilute solutions, under a given electromotive force, every ion moves through the liquid with a fixed velocity, dependent on its chemical nature but independent of the other ions. The conductivity, then, may be represented as the sum of two factors, related to each

[1] Z. physik. Chem., **39**, 613 (1902); **43**, 239 (1903).
[2] Pogg. Ann., **99**, 177 (1856).
[3] *Ibid.*, **103**, 466 (1858).
[4] Ann. Chim. Phys. [4], **14**, 157 (1868); [4], **21**, 264 (1870); [4], **22**, 361 (1871).
[5] Wied. Ann., **4**, 503 (1878).
[6] *Ibid.*, **6**, 1, 145 (1879).

other as the transport numbers of anion and cation. If the constant maximum conductivity and the transport numbers are known, the absolute velocity of either ion can be easily calculated.

This did not at once lead to increased activity in the determination of transport numbers. Kuschel[1] and Lenz[2] investigated a few salts, using a slightly modified form of the Hittorf apparatus.

In 1888, wishing to test further Kohlrausch's law, Loeb and Nernst[3] devised an apparatus for determining transport numbers, which did away entirely with porous diaphragms. It was essentially a Gay-Lussac burette provided near the top with a side tube for the reception of the cathode. Instead of the usual silver voltameter, they employed a galvanometer and Clark element in measuring the current. They determined the transport number of the silver ion in 8 salts and calculated its absolute velocity from their conductivity measurements. They found that the velocity, as calculated from the various salts, was constant to within the limits of experimental error.

The work of Chassy[4] needs only to be mentioned. Kistiakowsky,[5] in his determinations of transport numbers, used an extremely simple form of apparatus. It consisted merely of a vertical tube with a double bend near the top. His voltmeter is distinctive, the current being measured by determining volumetrically the amount of metal that had been dissolved from a silver anode.

Bein[6] carried out quite an extensive investigation on the effect of membranes and of temperature on transport numbers. He found that porous clay plates had no effect on the relative velocities of the ions, but that fish bladder retarded the cation. With increase in temperature the ions tend to move with equal velocities.

Lusanna[7] devised an apparatus of an entirely new form.

[1] Wied. Ann., **13**, 289 (1881).
[2] Mem. Acad. Imp. St. Petersb., [7], **30** (1882).
[3] Z. physik. Chem., **3**, 948 (1888).
[4] Ann. Chim. Phys., [6], **21**, 241 (1890).
[5] Z. physik. Chem., **6**, 97 (1890).
[6] Wied. Ann., **46**, 29 (1892).
[7] Att. Ist. Ven., [7], **3**, 1111 (1892); [7], **4**, 1568 (1893).

Three bulbs were connected by bent tubes in such a way as to form an S, and the whole apparatus, after being filled, was laid in the bath horizontally.

Rosenheim,[1] studying the composition of complex salts, subjected their solutions to electrolysis in two U-tubes connected by a rubber tube. Gordon[2] showed that the temperature coefficient of the transport numbers of cadmium sulphate and bromide is zero.

Schrader[3] and Hopfgartner[4] electrolyzed mixtures of salts and acids, to determine the relative velocities of different anions or cations.

Bein[5] again took up the problem and carried out a very elaborate series of investigations. He studied the effects of temperature and of concentration on the transport numbers of a large series of salts. He also gave special attention to the determination of the influence of dividing membranes. He found that, in general, they retarded the cation. From experiments with clay, parchment paper, fish bladder and gold beater's skin, he showed that the greatest change in velocity was produced by animal membranes, while porous clay divisions are almost without influence. He describes 5 forms of apparatus, all very complex.

Starck,[6] finding that the Hittorf apparatus with dividing membrane was not suitable for his purpose—the determination of the transport numbers for strong sulphuric acid—devised a simpler form, consisting of 3 U-tubes, connected by bent glass tubes.

In order to determine whether ternary electrolytes dissociate into complex ions, Noyes[7] made very careful determinations of the transport numbers for potassium sulphate and barium chloride and nitrate, in 0.1 N and 0.2 N solutions. He concluded that, even in the more concentrated solutions of potassium sulphate and barium nitrate, there are practically

[1] Z. anorg. Chem., **11**, 225 (1896).
[2] Z. physik. Chem., **23**, 469 (1897).
[3] Z. elek. Chem., **3**, 498 (1897).
[4] Z. physik. Chem., **25**, 115 (1898).
[5] *Ibid.*, **27**, 1 (1898); **28**, 439 (1899).
[6] *Ibid.*, **29**, 385 (1899).
[7] J. Am. Chem. Soc., **23**, 37 (1901).

no complex ions, while barium chloride solutions show evidence of the presence of considerable numbers of complex anions. In his investigation he used an apparatus consisting essentially of two U-tubes connected by rubber tubing.

Pfanhauser,[1] Rieger[2] and Bukschnewski[3] made some determinations of transport numbers. Pfanhauser was investigating the properties of nickel ammonium sulphate and used the Hittorf apparatus. Rieger, to study the electrolytic decomposition products of various complex salts, devised a rather complicated cell which, however, made possible a complete separation of the cathode and anode solutions after electrolysis.

Notwithstanding all the work that had been done in this field, all forms of apparatus thus far devised possessed very objectionable features. The solutions around the electrodes were kept separated by porous diaphragms, or by differences in specific gravity, and it was impossible to effect complete separation. Some of the most serious defects were overcome by Mather,[4] working with Jones, who used essentially an M-shaped tube divided into two equal compartments by a stop-cock of large bore. He made a few determinations of the transport numbers for silver nitrate and acetate and obtained satisfactory results.

Jahn[5] and his pupils undertook an extensive study of the effect of dilution on transport numbers. Their apparatus was quite similar to that of Hopfgartner. An Erlenmeyer flask served as anode compartment, while the cathode dipped into the further limb of a U-tube connected with a flask near the top of a lateral tube. They investigated solutions ranging in dilution from N/2 to N/300, of hydrochloric and nitric acids, silver nitrate, copper and cadmium sulphates, and the halogen salts of the alkalis, the alkaline earths and cadmium. They found that, in general, the transport numbers for most of the salts they studied reached a maximum, constant value at comparatively low dilutions. The relative

[1] Z. elek. Chem., **7**, 698 (1901).
[2] *Ibid.*, **7**, 863 (1901).
[3] Dissertation, Berlin, 1901.
[4] THIS JOURNAL, **26**, 473 (1901).
[5] Z. physik. Chem., **37**, 673 (1901).

velocity of the silver ion in the nitrate was practically constant between N/30 and N/214. The copper ion in copper sulphate increased in velocity as compared with the anion, but reached its maximum relative speed in a N/12 solution. The transport numbers for the cadmium salts, as had already been shown some time previously by Hittorf, changed rapidly with the concentration.

Owing to the limited capacity of their apparatus, they were unable to work with any high degree of accuracy with solutions more dilute than N/150. Steele and Denison,[1] however, shortly afterwards devised an apparatus in which they could electrolyze unlimited amounts of solution. It was very similar to the form used by Noyes, but was connected at the top with a reservoir from which fresh solution could be supplied as the electrolyzed portions were drawn off at the bottom. They worked with calcium sulphate, nitrate and chloride, in solutions containing about 0.0045 gram-molecular weight of the salt to the liter. They found, from their transport number and conductivity measurements, that the velocity of the calcium ion was the same, whether determined from the chloride or the nitrate, while calcium and potassium chlorides gave concordant results for the velocity of the chlorine ion.

Among the more recent investigations may be mentioned those of Huybrecht[2] and Wolf.[3] Both used the Hopfgartner-Jahn apparatus. Huybrecht studied magnesium sulphate and sulphuric acid. For this acid he found that the transport number of the hydrogen ion is constant for dilutions ranging between N/8 and N/80, and beyond N/105 it again has a constant, but somewhat higher value. Wolf obtained a negative temperature coefficient for the same ion in hydrochloric acid.

Noyes and Sammet[4] made an accurate determination of the equivalent conductivity of hydrogen, by determining its transport number in hydrochloric acid. Using the same method with sulphuric acid, Tower[5] finds that the relative velocity of

[1] J. Chem. Soc., **81**, 456 (1902).
[2] Dissertation, Berlin, 1901.
[3] *Ibid.*, 1903.
[4] J. Am. Chem. Soc., **24**, 944 (1903).
[5] *Ibid.*, **26**, 1039 (1904).

the anion increases markedly with dilution, from 1 N to 0.02 N solution, and has a large temperature coefficient between 8°, 20° and 32°.

The application of Hittorf's method to molten electrolytes by Lorenz and Fausti[1] is interesting. By the use of two porous clay cells, into which dipped carbon electrodes, they were able to show that in the electrolysis of a fused mixture of lead and potassium chlorides, the potassium migrates to the cathode and the lead to the anode, evidently as part of a complex anion.

Attention should be called to the papers of Stakelberg,[2] Burgess and Chapman[3] and McBain[4] on the determination of the relative velocities of complex ions which are partially dissociated into simpler ions.

3. *The Direct Determination of Ionic Velocities.*

The first direct determinations of the velocities of ions were made by Lodge[5] in 1886. He dipped the two ends of a tube filled with dilute hydrochloric acid into vessels containing sulphuric acid and barium chloride, respectively, and passed a current through it from the salt solution to the acid. By noting the time, and the distance from the two ends of the tube of the point at which the barium and sulphate ions met, he was able to calculate their velocities. To prevent diffusion as much as possible, he substituted later, for the hydrochloric acid, a dilute solution of acetic acid in gelatin. In a second series of experiments he observed the actual progress of the chlorine ion by using silver sulphate as indicator and tracing the advance of the precipitate of silver chloride.

Whetham[6] saw that Lodge's method had several objectionable features. The influence of the gelatin on the ionic velocities was entirely unknown, and no gelatin could be obtained so pure that it did not have a considerable conducting power of its own. In all methods based on the observation of the ad-

[1] Z. elek. Chem., **10**, 630 (1904).
[2] Z. physik. Chem., **23**, 493 (1897).
[3] J. Chem. Soc., **85**, 1305 (1904).
[4] Z. elek. Chem., **11**, 215, 961 (1905).
[5] Brit. Assn. Rep., 1886, p. 389.
[6] Phil. Trans. (A), 1893, p. 337.

vance of a precipitate, the precipitation of a part of the salt caused changes in concentration and, in aqueous solutions at least, mechanical disturbances. He therefore devised an apparatus in which the two solutions, which must have one ion in common while one of the other ions must possess a distinctive color, are held in a vertical tube, and the ionic velocity is determined by measuring the advance of the colored ion. To insure a uniform potential gradient, the two solutions must have about equal specific conductivities. Their densities must also be different in order to prevent mixing by diffusion. In a later series of experiments, Whetham[1] returns to the use of gelatin to prevent diffusion, and to precipitation methods to mark the advance of the ions. By making the quantity of indicator sufficiently small, the changes of concentration introduced by the last method become negligible. Lusanna[2] used Whetham's apparatus to study the effect of a magnetic field on ionic velocities.

Masson[3] next took up the problem. He used Whetham's method, but placed his tube horizontally and used only colored solutions as indicators. He carefully studied the conditions which must govern the choice of an indicator solution. The colored ion must travel at a specifically slower rate than the ion whose advance it marks, and the indicator must be of such a nature that it will not react chemically with the gelatin or the salt under investigation, giving rise to new ions. Under such conditions, experiment shows that the boundary line between the colored and the colorless zones is very sharp, and Kohlrausch[4] and Weber[5] prove theoretically that there can be no mixture of the ions. In many cases, towards the end of the experiment, Masson noticed that cracks and flaws appeared in the gelatin, but this did not seem to affect the relative velocities of the moving boundaries.

A few years later, Steele[6] devised a method which overcame many of the objectionable features of the older ones. The use

[1] Phil. Trans. (A), 1895, p. 607.
[2] Att. Ist. Ven., [7], **4**, 1568 (1893).
[3] Phil. Trans. (A), **192**, 331 (1899).
[4] Wied. Ann., **62**, 209 (1897).
[5] Sitz. Berl. Akad., 1897, p. 936.
[6] Phil. Trans. (A), **198**, 105 (1902).

of gelatin, as he notes, is impracticable, for the fall in potential is not uniform; the methods of Whetham and Masson are limited by the necessity of employing colored indicators, almost all of which give precipitates with the alkaline earths and the heavy metals. In his apparatus the solution under investigation is held in a vertical tube, between columns of gelatin containing the indicator in solution. The progress of the bounding layer can be easily followed, if the two solutions have slightly different refractive powers. The choice of indicators is thus largely increased. Measurements with salts like magnesium sulphate in both gelatin and water showed that the ionic velocities were affected by the gelatin, but with the alkali chlorides and bromides the velocities seem to be independent of the medium through which the ions travel.

Steele's values did not agree as well as could be desired with the transport numbers determined by Hittorf's method, and Abegg and Gauss[1] suggested that it might be due to endosmose. Modifying Steele's apparatus in such a way that they could measure the amount of solution forced through the gelatin and thus make the proper correction for it, they obtained, with potassium chloride, values agreeing very closely with those of Hittorf.

Denison[2] has extended this investigation to various other salts. He reaches the following conclusions:

1. In water, when correction is made for endosmose, the transport numbers for the simple sodium and potassium salts, determined in this way, agree with Hittorf's values.

2. For salts which form complex ions, or hydrolyze, the two sets of values do not agree but show parallelism.

3. Solid gelatin decreases the velocity of the cation. High concentration seems to have the same effect. Liquid gelatin does not influence the ionic velocities.

In a very recent paper, Denison and Steele[3] describe an apparatus and method in which they have entirely discarded the use of gelatin. The solution under investigation is inclosed between layers of aqueous solutions of the indicators, usually

[1] Z. physik. Chem., 40, 737 (1902).
[2] *Ibid.*, 44, 575 (1903).
[3] Phil. Trans. (A), 1906, p. 449.

lithium chloride for the cation and sodium formate, acetate or benzene sulphonate for the anion. The lead cathode is covered with lead peroxide and surrounded with dilute acetic acid. The anode is of cadmium amalgam. A little lithium hydroxide in the anode chamber retains the hydrogen ions formed by the hydrolysis of the cadmium chloride. With this apparatus they determined the transport numbers for the chlorides of the alkalies and alkaline earths, the nitrate, sulphate, chlorate, bromate, bromide and iodide of potassium, the alkali hydroxides, and hydrochloric, nitric and sulphuric acids in 0.1 N and 0.02 N solutions, and have obtained values agreeing very satisfactorily with those obtained by Hittorf's method. They claim for their method just as great accuracy, and a very large saving in time and labor.

4. Other Methods for Determining the Migration Velocities of Ions.

Various other methods for determining migration velocities have from time to time been proposed.

Kummel,[1] who determined the transport numbers of the halides and sulphates of zinc and cadmium by the Hittorf method, also measured the electromotive forces of concentration elements of the type

$$Cd : 0.1\ N\ CdCl_2 : 0.01\ N\ CdCl_2 : Cd$$

and

$$Hg : HgCl : 0.1\ N\ CdCl_2 : 0.01\ N\ CdCl_2 : HgCl : Hg.$$

As shown by Nernst,[2] from the ratio of the electromotive forces of two such elements, the transport numbers for the soluble salt can easily be calculated. Kummel obtained values for zinc and cadmium chlorides and cadmium sulphate that agreed very well with those found by the Hittorf method.

Kendrick[3] determined the transport number of the anion of sulphuric acid, containing from 1.4 to 55 per cent of H_2SO_4, by measuring the electromotive forces of 3 types of concentration elements:

[1] Wied. Ann., 64, 655 (1898).
[2] Z. physik. Chem., 4, 129 (1889).
[3] Z. elek. Chem., 7, 52 (1900).

Pb : dil. H_2SO_4 : conc. H_2SO_4 : Pb;
H_2 : dil. H_2SO_4 : conc. H_2SO_4 : H_2;
PbO_2 : dil. H_2SO_4 : conc. H_2SO_4 : PbO_2.

McIntosh[1] shows that the ratio of the electromotive forces of concentration elements, with and without diffusion, is equal to the transport number, and by this means he determined the transference number of hydrogen. He used cells of the type—

H_2 : HCl : HgCl : HCl : H_2—without diffusion;
H_2 : HCl : HCl : H_2—with diffusion.

The values obtained from duplicate experiments differ rather widely, and McIntosh concludes that the method is not applicable to gas cells, but it has been pointed out that the mean of his determinations does not differ more from the value calculated from Kohlrausch's conductivity measurements, than do the results of the different investigators using Hittorf's method.

When the solution of a salt, like copper sulphate, is electrolyzed, the process will be normal so long as the current density is kept below a certain point, but as soon as this critical point is passed, secondary processes set in and gas is evolved at the cathode. Weber[2] offered a possible explanation. At the critical density the copper ions, which, under a given electromotive force move with a fixed velocity, are just able to carry over all the positive electricity, and if this critical density is known, the absolute velocity of the ions can be calculated. Weber electrolyzed various solutions, gradually increasing the current density till a sudden rise in resistance gave evidence of polarization. This, he assumed, showed that the critical density had been reached. Experiments with copper and cadmium sulphates and zinc nitrate, gave results which agreed quite well with those of Kohlrausch.

Sheldon and Downing,[3] using solutions of copper sulphate, increased the current density by gradually withdrawing the cathode, a cylinder of known diameter, from the solution. As soon as the critical density was reached, the copper ceased

[1] J. Phys. Chem., 2, 273 (1898).
[2] Z. physik. Chem., 4, 182 (1889).
[3] Phys. Rev., 1, 51 (1894).

to be deposited in bright, metallic form, and the line of demarcation between the bright and the dark deposit was found to be quite sharp. They were thus able to determine the area of the cathode at the critical density, and from this the current density itself and the velocity of the copper ion.

5. Ionic Velocities in Non-aqueous Solvents.

Until within the last 3 years, very few determinations of ionic velocities had been made in solvents other than water. Hittorf, in his extensive investigation of transport numbers, electrolyzed a few solutions in ethyl and amyl alcohol. Lenz has recorded some measurements that he made with cadmium iodide in mixtures of water and alcohol.

Cattaneo[1] determined the effect of glycerol, methyl, ethyl and amyl alcohols, and mixtures of ethyl alcohol, chloroform and ether, on the transport number of the chlorine ion in hydrochloric acid. He found in all cases that the influence of the solvent was very slight. Campetti[2] measured the transport numbers for lithium chloride and silver nitrate in ethyl alcohol. Whetham determined directly the velocity of the cobalt ion in alcoholic solutions of cobalt chloride and nitrate. Mather worked with silver nitrate in mixtures of ethyl alcohol and water.

Schlundt[3] carried out some experiments with silver nitrate in pyridine and acetonitrile. Silver nitrate has a great "affinity" for these two liquids, and crystallizes from pyridine with 2 and 3 molecules of the solvent. As Schlundt expected, the relative velocity of the silver ion increases with the dilution. This is analogous to the phenomena observed in aqueous solution, with those salts which come out of solution with water of crystallization; the transport number of the cation almost always increases with the dilution.

Roth[4] gives some unpublished determinations of transport numbers made by Hornbostel and Goldberger, in mixtures of ethyl alcohol and water, containing from 10 to 40 per cent of

[1] Rend. Acc. Lincei [5], **3**, 207 (2 sem., 1897); [5], **6**, 279 (1 sem., 1898).
[2] Il Nuovo Cimento, **35**, 225 (1894). Ref., Z. physik. Chem., **16**, 165 (1895).
[3] J. Phys. Chem., **6**, 159 (1902).
[4] Z. physik. Chem., **42**, 219 (1903).

alcohol. Eisenstein[1] also worked along this line. From sodium chloride, the transport number of the chlorine ion increases with the amount of alcohol, but is unaffected by dilution. Goldberger's results with barium chloride are given below: v = the number of liters of solution containing a gram-molecular weight of the salt; a = the transport number of the anion:

	Percentage of Alcohol.					
	0 per cent.	10 per cent.	20 per cent.	25 per cent.	30 per cent.	40 per cent.
v.	a.	a.	a.	a.	a.	a.
30	0.543	0.531	0.540	0.549		0.536
60	0.548	0.536	0.543	0.551	0.545	0.536
90	0.553	0.545	0.547	0.550		0.536
120	0.554	0.546				0.536

The addition of small quantities of alcohol to the aqueous solution produces a lowering of the transport number, but as the proportion of alcohol is increased the relative velocity of the chlorine ion also increases, and reaches a maximum value in the mixture containing 25 per cent of alcohol. A further addition of alcohol produces a steady decrease. The transport number also increases with the dilution.

The first systematic study of ionic velocities in non-aqueous solvents was made by Carrara.[2] He used three pieces of apparatus, two of which had been devised by earlier investigators, Hittorf and Loeb and Nernst, while the third, he claims, is a new form, although it is very similar to that of Jones and Mather. He determined the transport numbers for some 20 salts of copper, cadmium and lithium, in methyl alcohol and, comparing them with the corresponding values for aqueous solutions, reached the conclusion that the relative velocities of the ions of an electrolyte tend toward the same value, independent of the solvent.

Dempwolf,[3] shortly afterwards, also determined the transport numbers for a large number of salts in methyl alcohol, and found that the oxymethyl ion, $\overline{OCH_3}$, of sodium methylate, has a velocity about equal to that of the chlorine ion.

[1] Dissertation, Berlin, 1902.
[2] Gazz. chim. ital., **33**, I., 241 (1903).
[3] Physik. Z., **5**, 637 (1904).

Jones and Bassett,[1] with the same apparatus that has been used in the present investigation, measured the relative velocity of the anion of silver nitrate at 0° and 25° in water, methyl and ethyl alcohol, and mixtures of water and methyl alcohol. They draw the following conclusions from their work:

"The difference in the relative velocities observed in the pure solvents at 0° and 25°, become less as the temperature rises, and the velocities, therefore, tend toward equality. This has already been observed for pure solvents, but it does not hold in the ease of mixed solvents.

"The relative velocities are largely dependent on the nature of the solvent.

"In mixed solvents the relative velocities are dependent on both the temperature and the composition of the mixture."

One of the most interesting investigations ever carried out in this field is that of Franklin and Cady,[2] on the determination of transport numbers of various salts in liquid ammonia. With considerable ingenuity they so modified Steele's apparatus that they were able to use it, satisfactorily, with such a low-boiling solvent as ammonia. The lower part of the tube was closed by a thread of mercury. In determinations of the velocities of cations, this mercury thread served as anode, and the mercury ions thus formed as the indicators. For anions, picric acid was generally employed as indicator. They found that for sodium and potassium nitrates, and sodium chloride and bromide, the ionic velocities are independent of the concentration. As was to be expected from the dielectric constant and association factor of liquid ammonia, the results of their work showed that the unusually high conductivities of solutions in this liquid, observed by Cady,[3] were due, not to a large dissociation, but to the high velocities of the ions in this medium. From their determinations of transport numbers and Cady's conductivity measurements, they demonstrate that the conductivity of completely dissociated electrolytes in liquid

[1] THIS JOURNAL, **32**, 409 (1904).
[2] J. Am. Chem. Soc., **26**, 499 (1904).
[3] J. Phys. Chem., **1**, 707 (1897).

ammonia is 2.5 to 3 times as high as the corresponding values in water.

Equally interesting is the very recent work of Steele, McIntosh and Archibald[1] on the properties of the liquid halogen acids. They find that such compounds as ether, acetone, substituted ammonium salts and ketones, in general, dissolved in liquid hydrobromic acid, conduct the current very well. After satisfying themselves, by measuring the amount of hydrogen liberated during electrolysis, that these solutions obey Faraday's law, they determined the transport number of the cation at two dilutions. They conclude that liquid hydrobromic acid forms addition products with the solute, and that these dissociate into complex cations and simple bromine anions.

PART II.

EXPERIMENTAL.

Object of This Investigation.

This work is a direct continuation of the investigation carried out in this university two years ago by Jones and Bassett.[2] They wished, if possible, to trace a connection between the phenomena of minimum conductivity, first observed by Zelinsky and Krapiwin[3] and later extensively studied by Jones and Lindsay,[4] which solutions in certain mixtures of alcohol and water exhibit. Jones[5] and his students have extended the investigation of this problem to mixtures of other solvents, including acetone, and have obtained interesting results. It was, therefore, thought desirable to extend also the work of Jones and Bassett. The conductivity of silver nitrate and the transport number of its anion in binary mixtures of water, methyl alcohol, ethyl alcohol and acetone, have been determined at two temperatures, 0° and 25°. In their determination of transport numbers, Jones and Bassett worked with 0.1 N solutions, but, owing to the limited solubility of silver nitrate in acetone, and to the desira-

[1] Phil. Trans. (A), 1905, p. 99.
[2] THIS JOURNAL, **32**, 409 (1904).
[3] Z. physik. Chem., **21**, 35 (1896).
[4] THIS JOURNAL, **28**, 329 (1902).
[5] *Ibid.*, **32**, 521 (1904); **34**, 481 (1905).

bility of having comparable values throughout, all measurements in this work have been made with 0.02 N solutions.

Solvents.

Water.—The water used in preparing the solutions was purified essentially by the method of Jones and Mackay.[1] Ordinary distilled water was twice redistilled from an acidified solution of potassium bichromate, and the steam from the second distillation passed through a boiling solution of barium hydroxide. It had, at 0°, a conductivity of about 1.0×10^{-6}.

Methyl Alcohol.—The purest obtainable product was boiled 1 to 2 days with lime, distilled and allowed to stand over anhydrous copper sulphate till needed. All distillations were made through a Singer fractionating head and a block-tin condenser, and the liquid was protected during distillation from the moisture in the air by means of a soda lime U-tube. To prevent any possibility of soda lime dust being drawn back into the liquid, the end of the tube nearest the bottle was covered with filter paper. The first and last portions of the distillate were always discarded. The mean conductivity at 0° = 0.8×10^{-6}.

Ethyl Alcohol.—The best commercial article was treated in the same manner as the methyl alcohol. Its conductivity at 0° was about 2.0×10^{-7}.

Acetone.—The acetone was allowed to stand over fused calcium chloride before using. Conductivity at 0° = 1.0×10^{-6}.

Mixed Solvents.—The mixture obtained by adding n cc. of Solvent A to $100-n$ cc. of Solvent B was designated as an "n per cent A—($100-n$) per cent B mixture." This method of preparing mixed solvents was deemed preferable to the more common method of diluting n cc. of Solvent A to 100 cc. with Solvent B. In the latter case it is always necessary to state which solvent is used as diluent, and the mixture must always be allowed to cool down to the temperature of the unmixed solvents before the final dilution to the mark on the measuring flask can be effected.

[1] THIS JOURNAL, 19, 83 (1897).

I. Conductivity.

Apparatus.—In making conductivity measurements, the usual Kohlrausch method, with Wheatstone bridge, induction coil and telephone receiver, was used. The bridge wire was of "manganin." The resistance coils were made by Leeds, of Philadelphia, and were calibrated to within 0.04 of 1 per cent.

The conductivity cells were of the type devised by Jones and Bingham[1] for use with volatile solvents, which, like acetone, attack rubber and wax. They differ from the simple Arrhenius cells in that the cup is closed by a ground glass stopper, into which are sealed with glass the tubes that carry the electrodes.

The electrodes were carefully cleansed with chromic acid and covered with platinum black, by electrolyzing a dilute solution of platinic chloride. All absorbed chlorine was removed with sodium hydroxide and the plates were washed with dilute hydrochloric acid and distilled water, dried and heated to redness in the flame of a blast-lamp. Electrodes thus treated gave a good tone minimum, did not appreciably absorb salts from their solutions and showed no tendency to cause the rapid oxidation of alcohol to acetic acid. When not in use the cells were filled with distilled water. Solutions were never allowed to stand in them longer than was necessary.

The 0° bath was of the form commonly used in this laboratory. A tin pail was filled with finely crushed ice and water and the cells were then packed into the ice as tightly as possible. The pail was placed into a larger, indurated filter bucket and the intervening space filled with finely crushed ice and water. Such a bath will maintain a temperature to within 0°.1 of 0° for hours. The 25° bath was a galvanized iron tub, lined on the outside with asbestos. The water in it was kept at a uniform temperature by means of a stirrer driven by a small hot-air motor, and could easily be kept to within 0°.1 of any desired temperature. The thermometers were graduated to 0°.1 and standardized. The burettes and measuring flasks

[1] THIS JOURNAL, 34, 481 (1905).

were all carefully calibrated by the method of Morse and Blalock.[1]

Preparation of Solutions.—The silver nitrate used in this work was obtained from Kahlbaum, and was perfectly neutral. It was finely pulverized, dried for several hours at 100°–105° and kept in a desiccator in the dark. Somewhat more of the salt than was necessary to prepare a 0.02 N solution was weighed into the solvent, and the exact concentration was determined by titration with a 0.04 N solution of ammonium sulphocyanate, with ferric ammonium sulphate as indicator. The sulphocyanate solution was standardized against a 0.04 N solution of silver nitrate, and weighed quantities of thoroughly dried potassium chloride, which had been especially purified in this laboratory for use in conductivity work. The solution whose conductivity was to be measured was then made exactly 0.02 N by the addition of the proper amount of solvent. From this mother-solution the other solutions were prepared by successive dilution. The N/800 and N/1200 solutions were prepared from the N/400.

Conductivity Measurements.—In measuring the conductivity of a solution, readings were always made with three different resistances, and the values given are the mean. Before using, the cells and electrodes were carefully dried and rinsed out with the solution whose conductivity was to be measured. The cell constants were determined with 0.02 N and 0.004 N solutions of pure potassium chloride. The molecular conductivity of the former was taken as 129.7 at 25°.

In the following tables, under v is given the concentration, expressed in number of liters of the solution containing a gram-molecular weight of the salt; under μ_v 0°, the molecular conductivity at 0°; and under μ_v 25°, the molecular conductivity at 25°.

The temperature coefficients are obtained by dividing the increase in conductivity per degree by the conductivity at 0°.

The values for the molecular conductivities in water and methyl and ethyl alcohols are obtained, by interpolation, from

[1] THIS JOURNAL, 16, 479 (1894).

the measurements of Jones and Bassett, and the temperature coefficients are calculated from those interpolated values.

Table I.—Molecular Conductivity of Silver Nitrate in a 75 Per Cent Water—25 Per Cent Acetone Mixture.

v.	μ_v 0°.	μ_v 25°.
50	38.97	78.79
100	40.91	81.82
200	42.36	85.70
400	41.65	85.00
800	43.24	88.24
1200	45.01	91.71

Conductivity of solvent at 0° = 1.15×10^{-6}.

Table II.—Molecular Conductivity of Silver Nitrate in a 50 Per Cent Water—50 Per Cent Acetone Mixture.

v.	μ_v 0°.	μ_v 15°.
50	31.31	62.97
100	31.72	64.34
200	33.00	67.69
400	33.74	68.50
800	34.32	71.12
1200	34.57	70.60

Conductivity of solvent at 0° = 1.66×10^{-6}.

Table III.—Molecular Conductivity of Silver Nitrate in a 25 Per Cent Water—75 Per Cent Acetone Mixture.

v.	μ_v 0°.	μ_v 25°.
50	30.79	53.04
100	34.59	60.05
200	36.49	63.81
400	38.75	68.34
800	40.35	70.63
1200	40.26	71.28

Conductivity of solvent at 0° = 2.06×10^{-6}.

Table IV.—Molecular Conductivity of Silver Nitrate in Acetone.

v.	μ_v 0°.	μ_v 25°.
125	7.93	10.08
200	8.18	10.36
400	8.58	11.57
800	9.64	12.08
1200	10.54	13.11

Conductivity of solvent at 0° = 1.0×10^{-6}.

Table V.—Molecular Conductivity of Silver Nitrate in Water, Acetone and Mixtures of These Solvents at 0°.

	Percentage of Acetone.				
v.	0 per cent. (Bassett.)	25 per cent.	50 per cent.	75 per cent.	100 per cent.
50	63.11	38.97	31.31	30.79	. .
100	63.71	40.91	31.72	34.59	. .
200	66.51	42.36	33.00	36.49	8.18
400	70.19	41.65	33.74	38.75	8.58
800	70.94	43.24	34.32	40.35	9.64
1200	70.65	45.01	34.57	40.26	10.54

Table VI.—Molecular Conductivity of Silver Nitrate in Water, Acetone and Mixtures of These Solvents at 25°.

	Percentage of Acetone.				
v.	0 per cent. (Bassett.)	25 per cent.	50 per cent.	75 per cent.	100 per cent.
50	111.62	78.79	62.97	53.04	. .
100	116.82	81.82	64.34	60.05	. .
200	121.16	85.70	67.69	63.81	10.36
400	125.27	85.00	68.50	68.34	11.57
800	125.73	88.24	71.12	70.63	12.08
1200	125.43	91.71	70.60	71.28	13.11

Table VII.—Temperature Coefficients of Conductivity of Silver Nitrate in Water, Acetone and Mixtures of These Solvents, 0°–25°.

	Percentage of Acetone.				
v.	0 per cent.	25 per cent.	50 per cent.	75 per cent.	100 per cent.
50	0.0307	0.0409	0.0404	0.0289	. .
100	0.0334	0.0400	0.0411	0.0294	. .
200	0.0329	0.0409	0.0430	0.0299	0.0107
400	0.0314	0.0416	0.0424	0.0305	0.0139
800	0.0309	0.0416	0.0429	0.0300	0.0101
1200	0.0310	0.0415	0.0417	0.0308	0.0097

The values in Tables I. to VI. are plotted as curves in Figs. I. and II., the abscissae representing the different percentages of acetone, and the ordinates the molecular conductivities. It

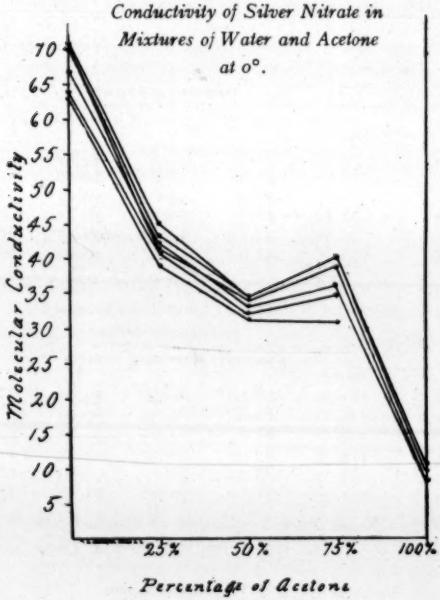

Fig. I.

will be seen that at 0°, for all dilutions but the lowest investigated, 0.02 N, there is a pronounced point of inflection that appears in the 75 per cent acetone mixture. At 25° it has al-

most disappeared, but still manifests itself at the higher dilutions. The curves are almost identical in form with those obtained by Jones and Bingham[1] for calcium nitrate, in mixtures of the same solvents.

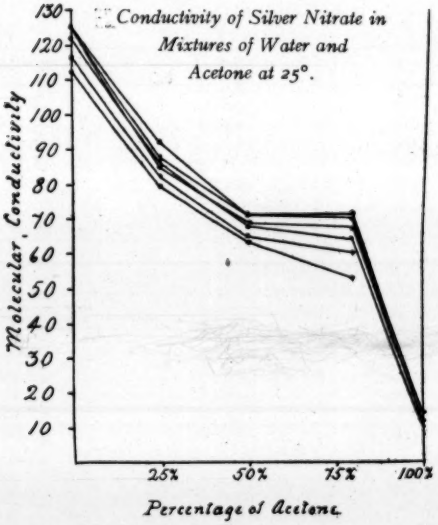

Fig. II.

Table VII. shows that the temperature coefficients increase with the proportion of acetone up to the 50 per cent mixture, but a further increase in the proportion of acetone produces a

[1] THIS JOURNAL, 34, 481 (1905).

rapid fall in the values for the temperature coefficients. With increase in concentration, the maximum value tends to shift to the 25 per cent acetone mixture. These results are also almost identical with those obtained by Jones and Bingham with calcium nitrate.

Table VIII.—Molecular Conductivity of Silver Nitrate in a 75 Per Cent Methyl Alcohol—25 Per Cent Ethyl Alcohol Mixture.

v.	μ_v 0°.	μ_v 25°.
50	32.39	45.69
100	38.01	54.09
200	44.94	64.40
400	47.09	67.72
800	50.45	72.85
1200	51.66	74.88

Conductivity of solvent at 0° $= 7.4 \times 10^{-7}$.

Table IX.—Molecular Conductivity of Silver Nitrate in a 50 Per Cent Methyl Alcohol—50 Per Cent Ethyl Alcohol Mixture.

v.	μ_v 0°.	μ_v 25°.
50	24.06	35.24
100	29.04	42.39
200	32.17	47.29
400	35.93	53.04
800	39.22	58.10
1200	40.06	59.68

Conductivity of solvent at 0° $= 3.1 \times 10^{-7}$.

Table X.—Molecular Conductivity of Silver Nitrate in a 25 Per Cent. Methyl Alcohol—75 Per Cent Ethyl Alcohol Mixture.

v.	μ_v 0°.	μ_v 25°.
50	17.45	26.54
100	20.78	31.89
200	23.40	36.41
400	26.45	41.32
800	28.38	44.71
1200	28.91	46.03

Conductivity of solvent at 0° $= 3.8 \times 10^{-7}$.

Table XI.—Molecular Conductivity of Silver Nitrate in Methyl and Ethyl Alcohols and Mixtures of These Solvents at 0°.

	Percentage of Ethyl Alcohol.				
v.	0 per cent. (Bassett.)	25 per cent.	50 per cent.	75 per cent.	100 per cent. (Bassett.)
50	41.10	32.39	24.06	17.45	11.79
100	46.73	38.01	29.04	20.78	13.61
200	52.49	44.94	32.17	23.40	15.61
400	57.89	47.09	35.93	26.45	17.64
800	. .	50.45	39.22	28.38	. .
1200	. .	51.66	40.06	28.91	. .

Table XII.—Molecular Conductivity of Silver Nitrate in Methyl and Ethyl Alcohols, and Mixtures of These Solvents at 25°.

	Percentage of ethyl alcohol.				
v.	0 per cent. (Bassett.)	25 per cent.	50 per cent.	75 per cent.	100 per cent. (Bassett.)
50	55.80	45.69	35.24	26.54	17.75
100	64.80	54.09	42.39	31.89	21.05
200	72.81	64.40	47.29	36.41	24.52
400	82.18	67.72	53.04	41.32	27.50
800	. .	72.85	58.10	44.71	. .
1200	. .	74.88	59.68	46.03	

Table XIII.—Temperature Coefficients of Conductivity of Silver Nitrate in Methyl and Ethyl Alcohol and Mixtures of These Solvents, 0°–25°.

	Percentage of Ethyl Alcohol.				
v.	0 per cent.	25 per cent.	50 per cent.	75 per cent.	100 per cent.
50	0.0143	0.0164	0.0186	0.0208	0.0202
100	0.0155	0.0169	0.0184	0.0214	0.0189
200	0.0155	0.0173	0.0188	0.0222	0.0203
400	0.0168	0.0175	0.0190	0.0225	0.0224
800	. .	0.0178	0.0192	0.0230	. .
1200	. .	0.0180	0.0196	0.0237	. .

Tables VIII. to XII. (Figs. III. and IV.) show that there is no trace of either a maximum or minimum, the curves being

Conductivity of Silver Nitrate in Mixtures of Methyl and Ethyl Alcohols at 0°.

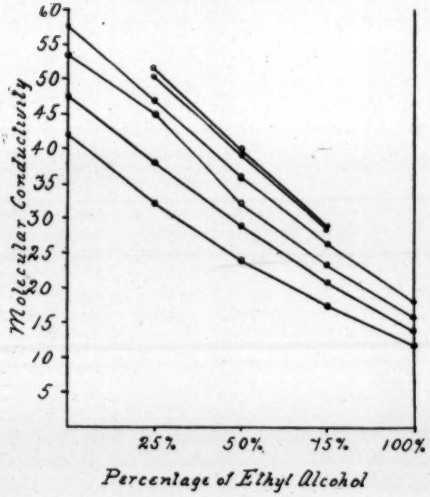

Fig. III.

straight lines to within the limits of experimental error. The temperature coefficients (Table XIII.) increase regularly with

the proportion of ethyl alcohol up to the 75 per cent mixture, and then remain practically constant, showing a slight tendency to drop.

Conductivity of Silver Nitrate in Mixtures of Methyl and Ethyl Alcohols at 25°.

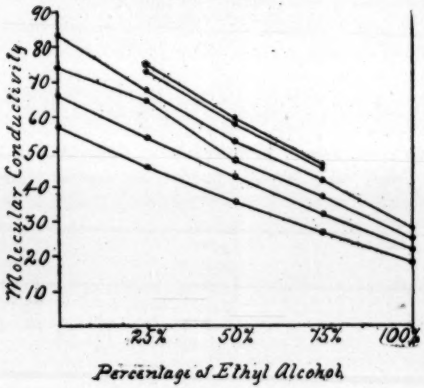

Fig. IV.

Table XIV.—Molecular Conductivity of Silver Nitrate in a 75 Per Cent Methyl Alcohol—25 Per Cent Acetone Mixture.

v.	μ_v 0°.	μ_v 25°.
50	40.45	53.81
100	46.36	64.24
200	55.60	73.65
400	63.98	83.08
800	65.62	92.69
1200	71.85	96.70

Conductivity of solvent at 0° $= 1.3 \times 10^{-6}$.

Table XV.—Molecular Conductivity of Silver Nitrate in a 50 Per Cent Methyl Alcohol—50 Per Cent Acetone Mixture.

v.	μ_v 0°.	μ_v 25°.
50	38.46	45.94
100	48.31	61.69
200	58.22	68.61
400	67.87	83.88
800	77.83	100.90
1200	81.57	100.40

Conductivity of solvent at 0° = 1.36×10^{-6}.

Table XVI.—Molecular Conductivity of Silver Nitrate in a 25 Per Cent Methyl Alcohol—75 Per Cent Acetone Mixture.

v.	μ_v 0°.	μ_v 25°.
50	25.49	28.40
100	33.67	37.78
200	42.42	47.00
400	51.50	59.87
800	63.19	75.12
1200	66.71	78.19

Table XVII.—Molecular Conductivity of Silver Nitrate in Methyl Alcohol, Acetone and Mixtures of These Solvents at 0°.

	Percentage of Acetone.				
v.	0 per cent. (Bassett.)	25 per cent.	50 per cent.	75 per cent.	100 per cent.
50	41.10	40.45	38.46	25.49	. .
100	46.73	46.36	48.31	33.67	. .
200	52.49	55.60	58.22	42.42	8.18
400	57.89	63.98	67.87	51.50	8.58
800	. .	65.62	77.83	63.19	9.64
1200	. .	71.85	81.57	66.71	10.54

Table XVIII.—Molecular Conductivity of Silver Nitrate in Methyl Alcohol, Acetone and Mixtures of These Solvents at 25°.

	Percentage of Acetone.				
v.	0 per cent. (Bassett.)	25 per cent.	50 per cent.	75 per cent.	100 per cent.
50	55.80	53.81	45.94	28.40	. .
100	64.80	64.24	61.69	37.78	. .
200	72.81	73.65	68.61	47.00	10.36
400	72.18	83.08	83.88	59.87	11.57
800	. .	92.69	100.90	75.12	12.08
1200	. .	96.70	100.40	78.19	13.11

Table XIX.—Temperature Coefficients of Conductivity of Silver Nitrate in Methyl Alcohol, Acetone and Mixtures of These Solvents, 0°–25°.

	Percentage of Acetone.				
v.	0 per cent.	25 per cent.	50 per cent.	75 per cent.	100 per cent.
50	0.0143	0.0132	0.0078	0.0046	. .
100	0.0155	0.0154	0.0119	0.0049	. .
200	0.0155	0.0130	0.0071	0.0068	0.0107
400	0.0168	0.0119	0.0119	0.0065	0.0139
800	. .	0.0165	0.0119	0.0076	0.0101
1200	. .	0.0138	0.0092	0.0069	0.0097

A study of Tables XIV. to XVIII. (Figs. V. and VI.) shows that at 0°, at the higher dilutions, silver nitrate in mixtures of methyl alcohol and acetone gives a maximum that almost disappears at 25°, although still evident in the more dilute solutions. The maximum appears in the 50 per cent

mixture. Here again the results are very similar to those found for calcium nitrate by Jones and Bingham, although silver nitrate does not, like the calcium salt, show, within the

Conductivity of Silver Nitrate in Mixtures of Methyl Alcohol and Acetone at 0°.

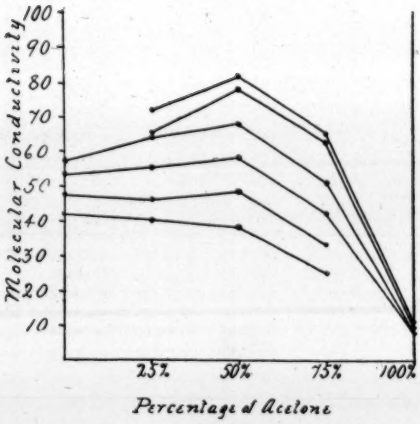

Fig. V.

limits of the dilutions investigated, any maximum in the 25 per cent acetone mixture.

The temperature coefficients (Table XIX.) exhibit a pro-

nounced maximum in the 75 per cent acetone mixture. This applies equally well to calcium nitrate.

Conductivity of Silver Nitrate in Mixtures of Methyl Alcohol and Acetone at 25°.

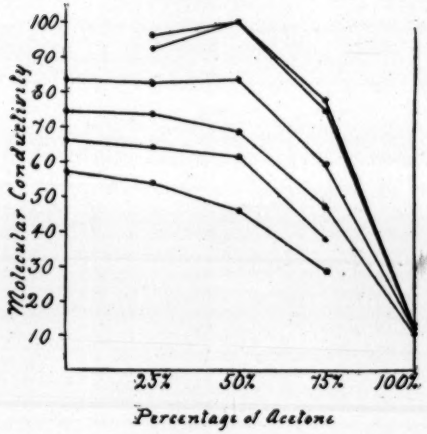

Fig. VI.

Table XX.—Molecular Conductivity of Silver Nitrate in a 75 Per Cent Ethyl Alcohol—25 Per Cent Acetone Mixture.

v.	μ_v 0°.	μ_v 25°.
50	15.86	22.39
100	19.90	28.38
200	25.06	33.64
400	27.40	39.82
800	31.51	46.30
1200	32.85	49.04

Conductivity of solvent at 0° $= 2.4 \times 10^{-7}$.

Table XXI.—Molecular Conductivity of Silver Nitrate in a 50 Per Cent Ethyl Alcohol—50 Per Cent Acetone Mixture.

v.	μ_v 0°.	μ_v 25°.
50	16.91	21.42
100	22.13	28.12
200	25.72	33.64
400	33.55	43.49
800	40.51	53.51
1200	43.90	58.69

Conductivity of solvent at 0° $= 4.6 \times 10^{-7}$.

Table XXII.—Molecular Conductivity of Silver Nitrate in a 25 Per Cent Ethyl Alcohol—75 Per Cent Acetone Mixture.

v.	μ_v 0°.	μ_v 25°.
50	13.38	16.36
100	17.42	23.06
200	22.20	27.60
400	29.80	.
800	37.84	45.80
1200	43.76	55.33

Conductivity of solvent at 0° $= 4.4 \times 10^{-7}$.

Table XXIII.—Molecular Conductivity of Silver Nitrate in Ethyl Alcohol, Acetone and Mixtures of These Solvents at 0°.

	Percentage of Acetone.				
v.	0 per cent. (Bassett.)	25 per cent.	50 per cent.	75 per cent.	100 per cent.
50	11.79	15.86	16.91	13.38	. .
100	13.61	19.90	22.13	17.42	. .
200	15.61	25.06	25.72	22.20	8.18
400	17.64	27.40	33.55	29.80	8.58
800	. .	31.51	40.51	37.84	9.64
1200	. .	32.85	43.90	43.76	10.54

Table XXIV.—Molecular Conductivity of Silver Nitrate in Ethyl Alcohol, Acetone and Mixtures of These Solvents at 25°.

	Percentage of Acetone.				
v.	0 per cent. (Bassett.)	25 per cent.	50 per cent.	75 per cent.	100 per cent.
50	17.75	22.39	21.42	16.36	. .
100	21.05	28.38	28.12	23.06	.
200	24.52	33.64	33.64	27.60	10.36
400	27.50	39.82	43.49	. .	11.57
800	. .	46.30	53.51	45.80	12.08
1200	. .	49.04	58.69	55.33	13.11

Table XXV.—Temperature Coefficients of Conductivity of Silver Nitrate in Ethyl Alcohol, Acetone and Mixtures of These Solvents, 0°–25°.

	Percentage of Acetone.				
v.	0 per cent.	25 per cent.	50 per cent.	75 per cent.	100 per cent.
50	0.0202	0.0165	0.0107	0.0089	. .
100	0.0189	0.0170	0.0108	0.0130	. .
200	0.0203	0.0137	0.0123	0.0097	0.0107
400	0.0224	0.0181	0.0118	. .	0.0139
800	. .	0.0188	0.0128	0.0084	0.0101
1200	. .	0.0197	0.0134	0.0106	0.0097

The similarity of the curves (Figs. VII. and VIII.) plotted from the values given in Tables XX. to XXIV., to the corresponding curves obtained by Jones and Bingham for calcium nitrate, is even more striking than in the case of the methyl alcohol and acetone mixtures. A pronounced minimum manifests itself at both 0° and 25°, appearing in the 25 per cent acetone mixture in the more concentrated solutions, and shifting, with increase in dilution, through the 50 per cent to the 75 per cent mixture.

As with calcium nitrate, the temperature coefficients (Table XXV.) show a minimum in the 75 per cent mixture.

In view of the great similarity in conductivity phenomena

exhibited by silver and calcium nitrates, in mixtures of water and of methyl and ethyl alcohols with acetone, it is interesting to know whether this is also true of solutions of the two salts in mixtures of water with the alcohols. By comparing the

Conductivity of Silver Nitrate in Mixtures of Ethyl Alcohol and Acetone at 0°.

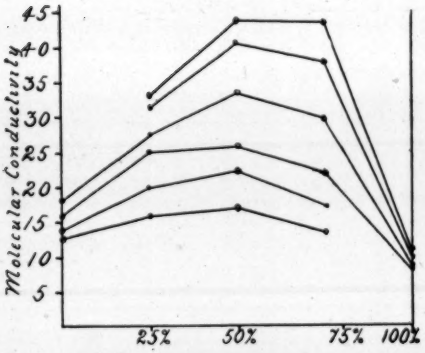

Fig. VII.

values for calcium nitrate in these mixtures, obtained by Jones and Carroll,[1] with the corresponding values for the silver salt which had been obtained by Jones and Bassett, it is seen

[1] This Journal, 32, 521 (1904).

that in mixtures of ethyl alcohol with water the conductivity curves for both salts are of the same form, showing no marked minimum, but exhibiting a tendency towards one in the 75 per

Conductivity of Silver Nitrate in Mixtures of Ethyl Alcohol and Acetone at 25°.

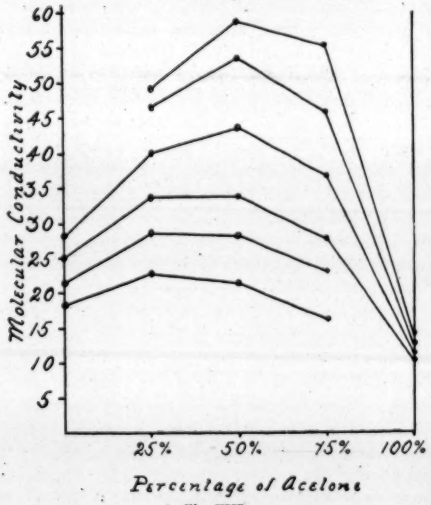

Fig. VIII.

cent alcohol mixture. In mixtures of methyl alcohol with water, however, while silver nitrate gives a very marked minimum in the 50 per cent mixture, the calcium salt does not.

Jones and Carroll did not work with dilutions greater than N/256, and it is quite possible that more dilute solutions would show a minimum.

II. Migration Velocity.

Apparatus.—The apparatus used in this investigation for the determination of the relative velocities of the ions of silver nitrate was devised by Jones and Bassett.[1] It is a modification of the form Mather[2] devised while working with Jones. The two outer limbs are 20 cm. long and 2 cm. in diameter and are connected 3 cm. below the stoppers, by a U-tube 1.5 cm. in diameter. Each arm of the U-tube is 10 cm. long, and at the center of it is a stop-cock of large bore (1 cm.). Into the electrodes, made of disks of pure silver, is riveted a short piece of stout platinum wire, which is then sealed into thick-walled glass tubes of 2 mm. bore. The exposed end of the platinum wire on the under side of the electrode is covered with fusion glass. The tubes carrying the electrodes are forced through holes bored into the ground-glass stoppers, which close the upper ends of the limbs of the apparatus. They are held firmly in place by pieces of rubber tubing. To prevent the solution from coming in contact with this rubber tubing, rings or flanges are blown on the glass tubes at the place where they enter the stopper, and are ground with carborundum to fit tightly into the holes in the stopper. To the limbs of the apparatus, just below the stoppers, are attached small, graduated tubes, 3 mm. in diameter, extending outward and upward. It was found, especially with alcohol and acetone solutions, that when the apparatus was placed in the 25° bath, a small quantity of gas always collected under the stopper and forced out some of the liquid through the side tubes. To prevent loss of solution from this source, the capacity of the side tubes was increased by attaching to them, by means of short pieces of thick rubber tubing, glass tubes of the same diameter with bulbs blown in them. An ordinary straight calcium chloride tube of small size answers the purpose very well.

[1] THIS JOURNAL, 32, 429 (1904).
[2] *Ibid.*, 26, 473 (1901).

Electrical connection is made with the electrodes through the platinum wires riveted into them by filling the tubes which carry them with mercury.

The advantages of this form of apparatus are evident. It is easily made and handled. It is perfectly symmetrical, so that either side can be used as cathode chamber. All danger of diffusion is done away with and no membrane is necessary. The stoppers being at the top, there can be no leakage, its comparatively large capacity, about 130 cc., which may be very accurately determined, making it possible to work with large quantities of solution. By means of the small side tubes the liquid in both arms can be very accurately leveled and, finally, the stop-cock at the center of the U-tube makes it possible to separate completely the cathode and anode solutions, and to rinse out the two sides as thoroughly as may be desired. By making the bore of the stop-cock sufficiently large, the resistance offered to the current is not materially increased.

The constant temperature bath was also constructed on the same general principles as that of Jones and Bassett.[1] A wooden box, 24 inches long, 14 inches wide and 10 inches deep, is lined to within half an inch of the top with thick, galvanized iron. On one side, 1.5 inches from the top, is a heavy, movable shelf, which serves to hold the voltameters. On the opposite side are wire hooks so arranged that, when the migration velocity apparatus is hung on them the bottom of the stoppers is level with the shelf. A section of the wooden bottom, 14 inches square, is removed and the contents of the bath can thus be heated by means of a small flame. The box is filled to the level of the shelf with water, which is kept at a uniform temperature by a small stirrer, driven by a hot-air motor. The bath proved very effective, being easily kept to within 0°.1 of the desired temperature. For measurements at 0°, the bath was filled with finely crushed ice, moistened with water, and the pieces of apparatus packed into the ice as tightly as possible. With a bath of these dimensions, 3 determinations can easily be carried out simultaneously.

The current used was always measured by means of a silver

[1] THIS JOURNAL, 32, 430 (1904).

voltameter. On a copper disk at the bottom of a weighing bottle was placed a platinum crucible, nearly filled with a 0.1 N solution of silver nitrate. Into this solution the anode, a bar of pure silver, was dipped by forcing it through a rubber stopper which served to close the weighing bottle. The anode was wrapped in a linen bag to prevent any detached particles from falling into the crucible. Connection with the circuit was established through copper wires soldered to the disk and the silver anode.

The binding posts on the bath, used to make electrical connection with the migration velocity apparatus and the voltameters, were placed on blocks of hard rubber, and in all the wiring special precautions were taken to prevent any leakage of current. Only heavily insulated copper wire was used, and at no point was it allowed to touch the bath, being held in position by porcelain insulators. Wherever two wires were placed near each other, they were further insulated by slipping a piece of rubber tubing over them.

Migration Velocity Measurements.—All the solutions used in this work were made up approximately 0.02 N, their exact concentration being determined by titration with a solution of ammonium sulphocyanate, which had been standardized in the manner described under "conductivity measurements."

Before every experiment the crucibles of the voltameters were treated with boiling nitric acid, fused acid potassium sulphate and boiling water. They were then heated to redness and weighed. After such treatment the silver was always deposited in a very adherent form, and could easily be washed without danger of loss. At the conclusion of the experiment the crucibles were rinsed out, allowed to stand over night full of distilled water, again rinsed out, dried from 30–60 minutes at 110°–115° and cooled in a desiccator.

To determine the capacity of each arm of the migration velocity apparatus, the stoppers were placed in position, the stop-cock closed, and each side filled from a burette to the zero mark on the small side tubes. To effect this, the burette was provided with a long, slender false tip, which could reach to the bottom of the side tubes.

To fill the apparatus with the solution to be electrolyzed, both stoppers were placed in position and one of the side tubes closed with a Bunsen valve. The other was connected by a piece of rubber tubing to a glass tube passing through a two-holed stopper to the bottom of the flask containing the solution. Through the other hole of the stopper passed a short glass tube connected with a soda lime U-tube. The end of the soda lime tube nearest the flask was covered with filter paper. By blowing through this tube, the solution could be forced over into the apparatus. The side tube was closed with a second Bunsen valve, the apparatus placed in the bath, and the current passed through the solution. The electrolysis was allowed to proceed till a sufficient amount of silver had been deposited in the voltameter, usually from 0.5–0.1 gram. The liquid in both arms was then carefully leveled, the stop-cock turned, and the cathode and anode solutions filtered through glass wool into 250 cc. measuring flasks and diluted nearly to the mark with the water used to rinse out the apparatus. After standing several hours, usually over night, the solutions were diluted to exactly 250 cc., and 100 cc. portions were titrated for their silver contents. Knowing the concentration of the solution before the electrolysis, the capacity of each arm of the apparatus, the amount of silver in the cathode solution after the electrolysis, and the amount of silver deposited in the voltameter, the relative migration velocity a of the anion was calculated from the equation

$$a = \frac{\text{loss of silver on cathode side}}{\text{silver deposited in voltameter}}.$$

To determine whether there had been any loss of silver by deposition of the peroxide on the anode, or from impurities in the electrodes, the anode solutions were also titrated.

Two different currents were used : one of 72 volts, furnished by a battery of storage cells, and one of 110 volts, supplied from the University power house. The current of lower voltage gave uniformly better results. The silver was usually deposited in beautiful needles on the cathode but, in some cases, especially where the current density was relatively high, the

deposit was more or less dark and of a spongy character. A thin covering of silver peroxide was generally deposited on the anode, and the analysis of the solution after the electrolysis usually showed that there had been a loss of from 0.5–1.0 per cent of silver. Some of the solutions offered a very great resistance to the passage of the current, and the electrolysis had to be continued from 12–20 hours. As it was impracticable, when working at 25°, to let the electrolysis proceed over night, it was attempted to use the city current of 220 volts which, however, was subject to rapid and irregular fluctuations all the way from 180–250 volts, but all such attempts were unsuccessful. The silver came down on the cathode in a very unsatisfactory form; there was a considerable deposition of peroxide on the anode, with a loss of silver of from 5–10 per cent, and the values obtained for the transport numbers from duplicate experiments did not show satisfactory agreement.

The acetone and alcohol solutions attacked, to a slight extent, the grease used to lubricate the stoppers and stop-cock, as was shown by the faint turbidity produced on diluting with water, but this source of error was not sufficient to affect the results materially.

The current never exceeded 0.005 ampere, and in some cases was as low as 0.001 ampere.

In the following tables, m_1 = the concentration of the solution before the electrolysis, expressed in fractions of gram-molecular weights of the salt contained in one liter of the solution; m_2 = concentration of the cathode solution after electrolysis; v = weight of silver in grams, deposited in the voltameter; and a = the transport number of the anion.

Table XXVI.—Relative Velocity of the Anion of Silver Nitrate in Water at 0°.

m_1.	m_2.	v.	a.
0.01999	0.01499	0.0657	0.563
0.01999	0.01464	0.0679	0.562
0.01984	0.01194	0.1014	0.557
0.01999	0.01488	0.0647	0.541

Table XXVII.—Relative Velocity of the Anion of Silver Nitrate in Water at 0°, as Determined by Different Observers.

m_1.	a.	
0.1	0.5409	(Mather)
0.102	0.5628	(Jones and Bassett)
0.025	0.5377	(Mather)
0.025	0.5383	(Loeb and Nernst)
0.02	0.555	(Jones and Rouiller)

The value that we obtained is higher than that given by Mather, and by Loeb and Nernst for solutions of about the same concentration, while Jones and Bassett found, with a 0.1 N solution, a value higher than our own for the more dilute solution.

Table XXVIII.—Relative Velocity of the Anion of Silver Nitrate in a 75 Per Cent Water—25 Per Cent Methyl Alcohol Mixture at 0°.

m_1.	m_2.	v.	a.
0.02036	0.01545	0.0671	0.546
0.02036	0.01573	0.0607	0.544
0.02030	0.01540	0.0628	0.549
0.02030	0.01551	0.0656	0.532
0.02030	0.01496	0.0703	0.541

Table XXIX.—Relative Velocity of the Anion of Silver Nitrate in a 50 Per Cent Water—50 Per Cent Methyl Alcohol Mixture at 0°.

m_1.	m_2.	v.	a.
0.02079	0.01784	0.0399	0.541
0.02079	0.01741	0.0418	0.576
0.02069	0.01753	0.0420	0.551
0.02069	0.01723	0.0437	0.564

Table XXX.—Relative Velocity of the Anion of Silver Nitrate in a 25 Per Cent Water—75 Per Cent Methyl Alcohol Mixture at 0°.

m_1.	m_2.	v.	a.
0.02016	0.01379	0.0848	0.514
0.02016	0.01561	0.0763	0.536

Table XXXI.—Relative Velocity of the Anion of Silver Nitrate in Methyl Alcohol at 0°.

m_1.	m_2.	v.	a.
0.02001	0.01483	0.0632	0.562
0.02001	0.01521	0.0629	0.559
0.02001	0.01479	0.0662	0.563

Table XXXII.—Relative Velocity of the Anion of Silver Nitrate in Water at 25°.

m_1.	m_2.	v.	a.
0.01999	0.01073	0.1211	0.544
0.01999	0.01128	0.1202	0.536
0.01999	0.01070	0.1155	0.543
0.02003	0.01069	0.1194	0.539

For the sake of comparison, the following table has been prepared :

Table XXXIII.—Relative Velocity of the Anion of Silver Nitrate in Water at Various Temperatures, as Determined by Different Observers.

t.	m.	a.	
11°.2	2.22	0.468	(Hittorf)
19°	2.02	0.478	"
18°.4	1.09	0.495	"
18°.8	0.87	0.510	"
75°–97°	0.49–0.64[1]	0.513	(Bein)
9°.6–19°.2	0.39–0.024	0.5256	(Hittorf)
	0.18–0.27	0.520	(Wiedemann[2])
13°–15°	0.17[1]	0.525	(Bein)
20°	0.104	0.528	(Loeb and Nernst)
29°.1	0.1	0.5317	(Mather)
47°.4–47°.7	0.1	0.5279	"
25°	0.1	0.5285	(Jones and Bassett)
26°	0.0521	0.524	(Loeb and Nernst)
18°–19°	0.033–0.0047	0.529	(Jahn)
26°	0.025	0.5223	(Loeb and Nernst)
45°	0.025	0.5246	(Mather)
25°	0.020	0.540	(Jones and Rouiller)
15°	0.01891	0.531	(Kistiakowsky)
26°	0.0105	0.5235	(Loeb and Nernst)

[1] Only a rough approximation; Bein expresses the concentration of his solutions in terms of percentages of silver, but does not give the specific gravity of the solutions.

[2] Wiedemann does not give the temperature at which he worked.

The value for the transport number, as this table shows, increases with the dilution. The value which we obtained is considerably higher than that found by other observers.

Table XXXIV.—Relative Velocity of the Anion of Silver Nitrate in a 75 Per Cent Water—25 Per Cent Methyl Alcohol Mixture at 25°.

m_1.	m_2.	v.	a.
0.02002	0.01449	0.0753	0.522
0.02002	0.01436	0.0788	0.531
0.02002	0.01356	0.0817	0.534

Table XXXV.—Relative Velocity of the Anion of Silver Nitrate in a 50 Per Cent Water—50 Per Cent Methyl Alcohol Mixture at 25°.

m_1.	m_2.	v.	a.
0.02080	0.01548	0.0709	0.534
0.02080	0.01590	0.0683	0.531
0.02080	0.01498	0.0735	0.534

Table XXXVI.—Relative Velocity of the Anion of Silver Nitrate in a 25 Per Cent Water—75 Per Cent Methyl Alcohol Mixture at 25°.

m_1.	m_2.	v.	a.
0.02012	0.01410	0.0755	0.566
0.02012	0.01424	0.0758	0.572
0.02012	0.01382	0.0775	0.549

Table XXXVII.—Relative Velocity of the Anion of Silver Nitrate in Methyl Alcohol at 25°.

m_1.	m_2.	v.	a.
0.02031	0.01498	0.0653	0.581
0.02031	0.01410	0.0800	0.577
0.02031	0.01402	0.0759	0.559

Table XXXVIII.—Relative Velocity of the Anion of Silver Nitrate in Methyl Alcohol, as Determined by Different Observers.

t.	*m.*	*a.*	
		0.533	(Campetti[1])
25°	0.0093	0.523	(Carrara)
25°	0.10	0.5797	(Jones and Bassett)
25°	0.02	0.572	(Jones and Rouiller)

The results obtained both by Jones and Bassett and by ourselves are considerably higher than the values given by the two Italian chemists.

Table XXXIX.—Relative Velocity of the Anion of Silver Nitrate in Water, Methyl Alcohol and Mixtures of These Solvents.

	Percentage of Methyl Alcohol.				
t.	0 per cent.	25 per cent.	50 per cent.	75 per cent.	100 per cent.
0°	0.555	0.542	0.559	0.525	0.561
25°	0.540	0.529	0.533	0.562	0.572

The determinations of Jones and Bassett, working with 0.1 N solutions in mixtures of water and ethyl alcohol are given in the following table :

Table XL.—Relative Velocity of the Anion of Silver Nitrate in Water, Methyl Alcohol and Mixtures of These Solvents, as Determined by Jones and Bassett.

	Percentage of Methyl Alcohol.				
t.	0 per cent.	25 per cent.	50 per cent.	75 per cent.	100 per cent.
0°	0.5628	0.5379	0.5299	0.5673	0.5871
25°	0.5285	0.5538	0.6010	0.5902	0.5797

The values in Table XXXIX. are plotted as curves in Fig. IX. A study of this figure shows that at 0°, the addition of 25 per cent of alcohol to the solution produces a fall in the relative velocity of the anion, but as the proportion of alcohol is increased the value for the transport number of the $\overline{NO}_3$ ion

[1] Campetti's original paper was not available, and the abstract in the Z. physik. Chem. gives neither temperature nor concentration.

again increases. A still further addition of alcohol again produces a depression in the curve, while in pure alcohol the relative velocity of the anion reaches a maximum value. A similar succession of rises and falls in the curve for the transport number was observed by Goldberger[1] for barium chloride, in mixtures of water and ethyl alcohol. With 0.1 N solutions of silver nitrate, Jones and Bassett obtained a pronounced minimum in the 50 per cent methyl alcohol mixture. At 25° the curve shows that the addition of alcohol produces a slight low-

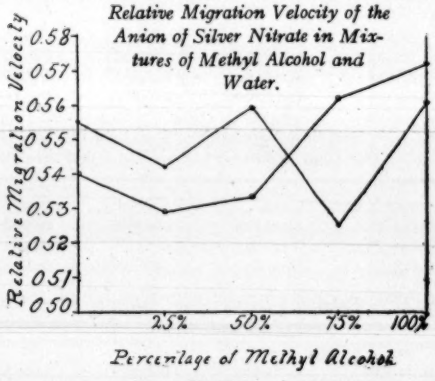

Fig. IX.

ering of the transport number, until the proportion of alcohol is raised to about 50 per cent. Further addition of alcohol produces a rapid increase in the relative velocity of the anion. Jones and Bassett, on the other hand, find that for the 0.1 N solution there is a sharp maximum in the 50 per cent mixture. A comparison of Tables XXXIX. and XL. shows that in solutions of different concentration the effect of the solvent on the migration velocities of the two ions is widely different.

[1] Roth: Z. physik. Chem., 42, 209 (1903).

Table XLI.—Relative Velocity of the Anion of Silver Nitrate in a 75 Per Cent Water—25 Per Cent Ethyl Alcohol Mixture at 0°.

m_1.	m_2.	v.	a.
0.02042	0.01605	0.0569	0.543
0.02042	0.01654	0.0527	0.537
0.02046	0.01427	0.0843	0.534
0.02046	0.01342	0.0925	0.543
0.02042	0.01582	0.0582	0.564

Table XLII.—Relative Velocity of the Anion of Silver Nitrate in a 50 Per Cent Water—50 Per Cent Ethyl Alcohol Mixture at 0°.

m_1.	m_2.	v.	a.
0.02073	0.01777	0.0369	0.549
0.02073	0.01810	0.0358	0.537
0.02073	0.01799	0.0361	0.541

Table XLIII.—Relative Velocity of the Anion of Silver Nitrate in a 25 Per Cent Water—75 Per Cent Ethyl Alcohol Mixture at 0°.

m_1.	m_2.	v.	a.
0.02052	0.01573	0.0588	0.576
0.02052	0.01593	0.0588	0.570
0.02052	0.01540	0.0616	0.593

Table XLIV.—Relative Velocity of the Anion of Silver Nitrate in Ethyl Alcohol at 0°.

m_1.	m_2.	v.	a.
0.02000	0.01569	0.0487	0.625
0.02000	0.01587	0.0494	0.610
0.02000	0.01542	0.0519	0.627

Table XLV.—Relative Velocity of the Anion of Silver Nitrate in a 75 Per Cent Water—25 Per Cent Ethyl Alcohol Mixture at 25°.

m_1.	m_2.	v.	a.
0.02064	0.01450	0.0820	0.528
0.02064	0.01467	0.0821	0.535
0.02064	0.01409	0.0821	0.545
0.01980	0.01556	0.0536	0.532
0.01980	0.01609	0.0530	0.517
0.01980	0.01589	0.0538	0.516

Table XLVI.—Relative Velocity of the Anion of Silver Nitrate in a 50 Per Cent Water—50 Per Cent Ethyl Alcohol Mixture at 25°.

m_1.	m_2.	v.	a.
0.02089	0.01590	0.0662	0.536
0.02089	0.01633	0.0649	0.521
0.02089	0.01581	0.0654	0.524

Table XLVII.—Relative Velocity of the Anion of Silver Nitrate in a 25 Per Cent Water—75 Per Cent Ethyl Alcohol Mixture at 25°.

m_1.	m_2.	v.	a.
0.02063	0.01603	0.0583	0.560
0.02063	0.01622	0.0579	0.563
0.02063	0.01600	0.0576	0.553

Table XLVIII.—Relative Velocity of the Anion of Silver Nitrate in Ethyl Alcohol at 25°.

m_1.	m_2.	v.	a.
0.02001	0.01717	0.0328	0.616
0.02001	0.01691	0.0364	0.633
0.02001	0.01672	0.0372	0.598

Table XLIX.—Relative Velocity of the Anion of Silver Nitrate in Ethyl Alcohol at Various Temperatures, as Determined by Different Observers.

t.	m.	a.	
3°.8–5°	0.150	0.573	(Hittorf)
20°	0.108	0.594	(Mather)
25°	0.076–0.101	0.5988	(Jones and Bassett)
25°	0.020	0.616	(Rouiller)

In ethyl alcohol also, as this table shows, the velocity of the anion increases with the dilution.

Table L.—Relative Velocity of the Anion of Silver Nitrate in Water, Ethyl Alcohol and Mixtures of These Solvents.

	Percentage of Ethyl Alcohol.				
	0 per cent.	25 per cent.	50 per cent.	75 per cent.	100 per cent.
0°	0.555	0.544	0.542	0.580	0.621
25°	0.540	0.529	0.527	0.559	0.616

As Table L. and Fig. X. show, at both 0° and 25° the relative velocity of the anion, in mixtures of ethyl alcohol with water, decreases slightly as the proportion of alcohol is increased, but reaches a minimum in the 50 per cent mixture.

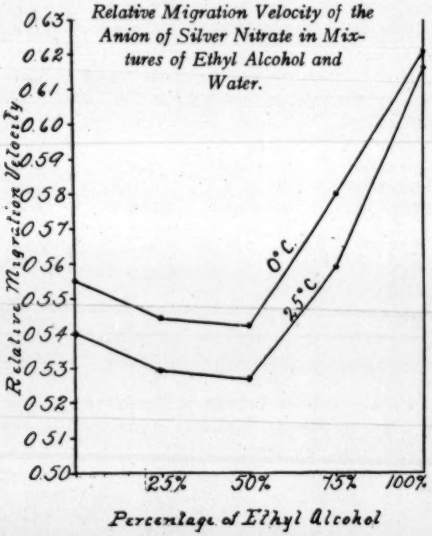

Fig. X.

From this point, increasing quantities of alcohol produce a very rapid rise in the relative velocity of the $\overline{NO_3}$ ion. With increasing temperature the two ions, in all these mixtures, tend to move with velocities that are more nearly equal.

Table LI.—Relative Velocity of the Anion of Silver Nitrate in a 75 Per Cent Water—25 Per Cent Acetone Mixture at 0°.

m_1.	m_2.	v.	a.
0.02061	0.01565	0.0677	0.537
0.02061	0.01534	0.0706	0.533

Table LII.—Relative Velocity of the Anion of Silver Nitrate in a 50 Per Cent Water—50 Per Cent Acetone Mixture at 0°.

m_1.	m_2.	v.	a.
0.02090	0.01601	0.0647	0.552
0.02090	0.01549	0.0688	0.561

Table LIII.—Relative Velocity of the Anion of Silver Nitrate in a 25 Per Cent Water—75 Per Cent Acetone Mixture at 0°.

m_1.	m_2.	v.	a.
0.02082	0.01598	0.0617	0.575
0.02082	0.01558	0.0647	0.579

It was found that the most concentrated solution of silver nitrate in acetone, that could be prepared by long-continued shaking of the salt with the liquid at room temperature, contained less than 0.01 gram-molecular weight of the salt to the liter. With such dilute solutions it was impracticable to make a determination of the transport number.

Table LIV.—Relative Velocity of the Anion of Silver Nitrate in a 75 Per Cent Water—25 Per Cent Acetone Mixture at 25°.

m_1.	m_2.	v.	a.
0.02061	0.01301	0.1023	0.528
0.02061	0.01275	0.1098	0.530
0.02061	0.01169	0.1139	0.528

Table LV.—Relative Velocity of the Anion of Silver Nitrate in a 50 Per Cent Water—50 Per Cent Acetone Mixture at 25°.

m_1.	m_2.	v.	a.
0.02110	0.01270	0.1106	0.540
0.02110	0.01301	0.1109	0.540
0.02110	0.01248	0.1092	0.543

Table LVI.—Relative Velocity of the Anion of Silver Nitrate in a 25 Per Cent Water—75 Per Cent Acetone Mixture at 25°.

m_1.	m_2.	v.	a.
0.02100	0.01517	0.0713	0.581
0.02100	0.01567	0.0706	0.559
0.02100	0.01518	0.0702	0.571

Table LVII.—Relative Velocity of the Anion of Silver Nitrate in Water, Acetone and Mixtures of These Solvents.

	Percentage of Acetone.				
t.	0 per cent.	25 per cent.	50 per cent.	75 per cent.	100 per cent.
0°	0.555	0.535	0.556	0.577	. .
25°	0.540	0.529	0.541	0.570	. .

The values in Table LVII. are plotted as curves in Fig. XI. There is a pronounced minimum in the 25 per cent acetone

Relative Migration Velocity of the Anion of Silver Nitrate in Mixtures of Water and Acetone.

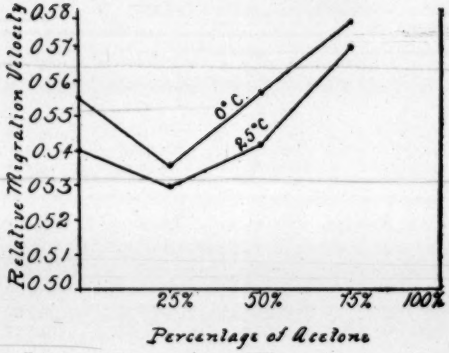

Fig. XI.

mixture. As in the mixtures with ethyl alcohol and water, the difference between the velocities of the anion and cation decreases with rise in temperature.

Table LVIII.—Relative Velocity of the Anion of Silver Nitrate in a 75 Per Cent Methyl Alcohol—25 Per Cent Ethyl Alcohol Mixture at 0°.

m_1.	m_2.	v.	a.
0.02004	0.01105	0.1139	0.576
0.02004	0.01023	0.1192	0.587

Table LIX.—Relative Velocity of the Anion of Silver Nitrate in a 50 Per Cent Methyl Alcohol—50 Per Cent Ethyl Alcohol Mixture at 0°.

m_1.	m_2.	v.	a.
0.01996	0.01407	0.0718	0.599
0.01996	0.01376	0.0755	0.583

Table LX.—Relative Velocity of the Anion of Silver Nitrate in Methyl and Ethyl Alcohols and Mixtures of These Solvents.

	Percentage of Ethyl Alcohol.				
t.	0 per cent.	25 per cent.	50 per cent.	75 per cent.	100 per cent.
0°	0.561	0.581	0.591	. .	0.621

The relative velocity of the anion in mixtures of methyl and ethyl alcohol, increases uniformly with the proportion of ethyl alcohol. This is entirely analogous to the results obtained in measuring the conductivities of solutions in mixtures of the two alcohols.

Table LXI.—Relative Velocity of the Anion of Silver Nitrate in a 75 Per Cent Methyl Alcohol—25 Per Cent Acetone Mixture at 0°.

m_1.	m_2.	v.	a.
0.02036	0.01084	0.1304	0.533
0.02036	0.01006	0.1378	0.536

Table LXII.—Relative Velocity of the Anion of Silver Nitrate in a 50 Per Cent Methyl Alcohol—50 Per Cent Acetone Mixture at 0°.

m_1.	m_2.	v.	a.
0.02038	0.01312	0.0934	0.569
0.02038	0.01276	0.0966	0.563

Table LXIII.—Relative Velocity of the Anion of Silver Nitrate in a 25 Per Cent Methyl Alcohol—75 Per Cent Acetone Mixture at 0°.

m_1.	m_2.	v.	a.
0.02037	0.01539	0.0580	0.627
0.02037	0.01498	0.0620	0.620

Table LXIV.—Relative Velocity of the Anion of Silver Nitrate in a 75 Per Cent Methyl Alcohol—25 Per Cent Acetone Mixture at 25°.

m_1.	m_2.	v.	a.
0.02020	0.01541	0.0583	0.584
0.02020	0.01545	0.0599	0.588
0.02020	0.01505	0.0617	0.563

Table LXV.—Relative Velocity of the Anion of Silver Nitrate in a 50 Per Cent Methyl Alcohol—50 Per Cent Acetone Mixture at 25°.

m_1.	m_2.	v.	a.
0.02028	0.01549	0.0556	0.613
0.02028	0.01570	0.0534	0.634
0.02028	0.01578	0.0498	0.609

Table LXVI.—Relative Velocity of the Anion of Silver Nitrate in Methyl Alcohol, Acetone and Mixtures of These Solvents.

	Percentage of Acetone.				
t.	0 per cent.	25 per cent.	50 per cent.	75 per cent.	100 per cent.
0°	0.561	0.534	0.566	0.623	. .
25°	0.572	0.578	0.619	. .	. .

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Table LXVI. (Fig. XII.) shows that in methyl alcohol and acetone the transport number of the anion has a minimum

Relative Migration Velocity of the Anion of Silver Nitrate in Mixtures of Methyl Alcohol and Acetone.

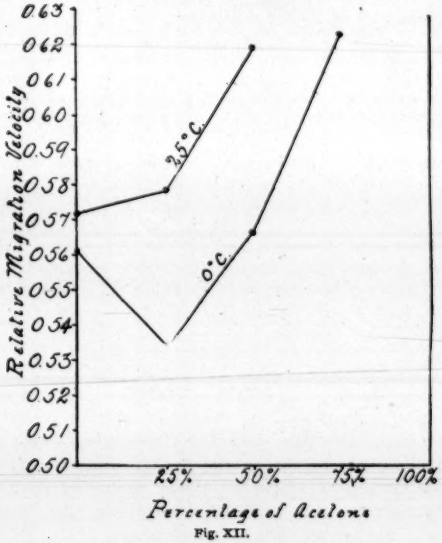

Fig. XII.

value, at 0°, in the mixture containing 25 per cent of acetone. At 25° the minimum has disappeared. It is interesting to note that in these mixtures the relative velocity of the anion increases with rise in temperature.

Table LXVII.—Relative Velocity of the Anion of Silver Nitrate in a 75 Per Cent Ethyl Alcohol—25 Per Cent Acetone Mixture at 0°.

m_1.	m_2.	v.	a.
0.02003	0.01421	0.0730	0.564
0.02003	0.01454	0.0690	0.580

Table LXVIII.—Relative Velocity of the Anion of Silver Nitrate in a 50 Per Cent Ethyl Alcohol—50 Per Cent Acetone Mixture at 0°.

m_1.	m_2.	v.	a.
0.02001	0.01451	0.0643	0.585
0.02001	0.01493	0.0634	0.586
0.02001	0.01461	0.0665	0.579

Table LXIX.—Relative Velocity of the Anion of Silver Nitrate in Ethyl Alcohol, Acetone and Mixtures of These Solvents.

	Percentage of Acetone.				
t.	0 per cent.	25 per cent.	50 per cent.	75 per cent.	100 per cent.
0°	0.621	0.572	0.583	. .	. .

In ethyl alcohol and acetone, there is a pronounced minimum in the relative velocity of the anion in the mixture containing 25 per cent of acetone.

PART III.

Discussion of Results.

Changes produced in the relative migration velocities, or transport numbers of the ions of an electrolyte, by varying the nature of the solvent, may be due to three causes:

1. Owing to some property peculiar to one of the ions, its velocity may be influenced by the solvent more than the velocity of the ion with the opposite charge.

2. Complex ions may be formed, which are more or less dissociated, according to the nature of the solvent, into simpler ions.

3. The ions may combine with the solvent itself.

That ions do combine with the solvent in many cases has been established, especially by the work of Jones and his pupils in this laboratory. But, if this is to affect the *relative*

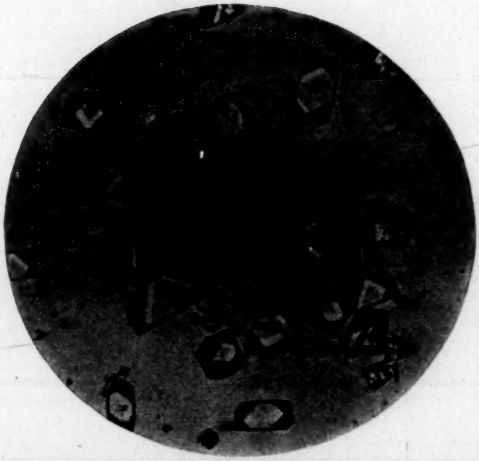

Plate I.

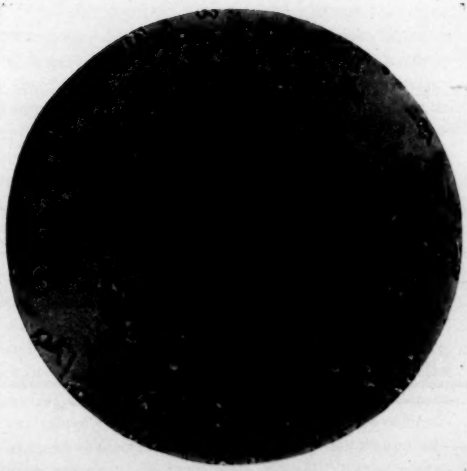

Plate II.

velocities of the positive and negative ions, the solvent must combine with only one ion, or *different* quantities of it must combine with anion and cation, respectively. This, in substance, is the view proposed by Jones and also by Kohlrausch.[1] "About every ion there moves an atmosphere of the solvent, whose dimensions are determined by the individual characteristics of the ions. . . . . The electrolytic resistance is a frictional resistance that increases with the dimensions of the atmosphere. The direct action between the ion and the outer portion of the solvent, diminishes as the atmosphere becomes of greater thickness. . . . . For a very sluggish ion there will be only the friction of water against water, and the electrolytic resistance will have the same temperature coefficient as the viscosity of the water, provided the atmosphere itself does not change its dimensions with the temperature. If, however, the atmosphere becomes, for example, smaller with increasing temperature, the temperature gradient of the conductivity might be greater than that of the fluidity. According to observations now at hand, this would seem to be the case for the slowest moving, univalent ion, Li."

It has been attempted to show experimentally that the solvent does, in some cases, unite with only one, or in greater quantities with one ion. Thus, Oppermann,[2] by electrolyzing silver acetate in a mixture of acetic acid and water, concluded that the ion $\overline{CH_3COO}$ carries with it 6 more molecules of water than the silver. Working along the same lines with silver nitrate in methyl alcohol and water, Lobry de Bruyn[3] obtained negative results. Morgan and Kanolt,[4] using essentially the apparatus devised by Jones and Bassett, thought they found that in mixtures of water and ethyl alcohol the cation of silver nitrate carries along with it 1 molecule of water more than the anion. Their experimental work is, however, far from convincing, and their erroneous statement that the results of Jones do not show whether it is the free ions that are combined with solvent molecules, could easily have been

[1] P. Roy. Soc., **71**, 338 (1903).
[2] Dissertation, Göttingen, 1901.
[3] Rec. Trav. Chim., **22**, 430 (1903).
[4] J. Am. Chem. Soc., **27**, 572 (1906).

avoided by simply reading the recent papers of Jones and Bassett.[1] In pyridine and water the silver ion carries, according to them, pyridine to the cathode.

The fact that the transport numbers of the ions of many simple binary electrolytes, where the possibility of the formation of complex ions is very doubtful, change with the dilution until they reach a constant value, is in harmony with the Kohlrausch view. That there is preferential combination of the solvent with one of the ions we cannot prove directly for pure solvents, but, if we arrange electrolytes in groups, according to the power of forming hydrates in solution, as determined by Jones and his co-workers, we find that, in general, *the power of forming hydrates is, in some way, dependent on the nature of the cation and more or less independent of the anion.* Thus, sodium, potassium and ammonium salts fall in the group showing the least tendency to form hydrates. Iron and aluminium salts form complex hydrates, while calcium, strontium and magnesium salts are intermediate between them and the alkali salts. If we compare these facts with the phenomena exhibited by transport numbers, we find that the relative velocities of the cations of salts with small power of hydration are practically independent of the concentration, while the transport numbers of such ions as calcium, strontium and magnesium, increase with the dilution. It is true that this may be due largely to the presence of complex ions in the more concentrated solutions, but the relative velocity of the cation of lithium chloride which, alone of the alkali chlorides crystallizes with water of crystallization, also increases considerably with the dilution. This can hardly be due to the presence of complex ions in the more concentrated solutions.

The data for transport numbers in non-aqueous solvents, at different dilutions, are too meagre to show whether this is true for other solvents than water. That it holds for silver nitrate in pyridine and acetonitrile has been shown by Schlundt.

Silver nitrate in water is a striking exception. The velocity of the anion increases with the dilution. It should be noted, however, that the nitrates of sodium and potassium exhibit

[1] THIS JOURNAL, **33**, 583 (1905); **34**, 346 (1906).

the same phenomena, although not quite so strikingly. The relative velocities of the cations of these salts decrease slightly with the dilution. It would seem, therefore, that in these salts it is the anion that is combined with the larger amount of the solvent.

Increase in temperature, as shown by Jones, would have a tendency to break up hydrates in solution. It has been found experimentally that, in most cases, raising the temperature increases the relative velocity of the slower ion.

That the relative ionic velocities for certain electrolytes are affected by the presence of complex ions, at least in the more concentrated solutions, is generally accepted. Reference need only be made to the classical case of cadmium iodide, which was first studied by Hittorf, and has since been the subject of a large number of investigations. As there is little probability that silver nitrate forms complex ions, this point will not be discussed in the present paper.

Finally, that the fluidity of the solvent affects the migration velocities is true beyond doubt, but how it affects the *relative* velocities we cannot as yet say. It is, of course, impossible to obtain solutions containing ions of only one kind and measure their viscosities, so that we are unable to determine, for any electrolyte in a given solvent, whether the friction of ion against solvent is greater for the cation than for the anion, or *vice versa*. In the present state of our knowledge, the influence of size and configuration on relative ionic velocities is also unknown. It may be stated that, in the course of this investigation, although working with solvents having such widely different fluidities as water, methyl and ethyl alcohols and acetone, it has not been possible to trace any connection between the transport numbers of the same ion and the fluidities of the solvents. This can be seen from the table given below. The values for the fluidities of the solvents are taken from the work of Jones and Bingham (see Table LXX.).

That there is any connection between the influence of the solvent on transport numbers and the nature of the charge carried by the ion, is very improbable. If there were any such connection, the influence of one solvent on different ions

with the same kind of charge, other things being equal, would always be in the same direction ; in other words, it would always increase the relative velocity of the anion, or *vice versa*. Here again, the lack of data for transport numbers of suffi-

Table LXX.—Relative Migration Velocity of the Anion of Silver Nitrate in Water, Methyl and Ethyl Alcohols and Acetone, with the Fluidity of These Solvents, at 0° and 25°.

	0°.		25°.	
Solvent.	Fluidity.	Transport No.	Fluidity.	Transport No.
Water	56.24	0.555	112.3	0.540
Methyl alcohol	122.20	0.561	176.7	0.572
Ethyl alcohol	53.88	0.621	90.35	0.616
Acetone	244.10	>0.620	308.9	>0.620

ciently dilute solutions in non-aqueous solvents, makes it impossible to draw any general conclusion as to the existence or non-existence of such a relation.

Since, from the increase with the dilution, of the relative velocity of the anion of silver nitrate in water, it would seem that the negative ion is combined with a greater quantity of the solvent, we should expect the addition to the solution of some "dehydrating agent," such as alcohol, would have the same effect as an increase in concentration in the water solution ; in other words, *a decrease in the relative velocity of the anion*. That this is true for ethyl alcohol up to the 50 per cent mixture, and that the increase is slightly more marked at 0° than at the higher temperature, as would be expected, is shown by Fig. X. As the relative velocity of the anion in pure alcohol is much larger than in water, increasing amounts of alcohol will tend to retard the cation, and beyond the 50 per cent mixture the effects of decreasing hydration are entirely masked and the relative velocity of the anion increases rapidly.

In this connection, attention should be called to the work of Lobry de Bruyn and Jungius[1] and of Bruni and Manuelli,[2] who have shown, by cryoscopic methods, that certain hydrated salts, when dissolved in organic solvents, retain part of their water of crystallization.

[1] Rec. Trav. Chim., **22**, 421 (1903).
[2] Z. Elek. Chem., **10**, 601 (1904).

Looking at Fig. IX., it will be seen that what has been said for ethyl alcohol and water is true of methyl alcohol and water at 25°. But the increase in the relative velocity of the cation with the addition of alcohol to the solvent is not so marked, and the influence in the opposite direction of increasing amounts of alcohol, already manifests itself in the 50 per cent mixture. The curve for the transport number of the anion at 0° shows a minimum in the 25 per cent mixture, but beyond the 50 per cent mixture it is abnormal. No explanation for this can as yet be offered.

Although we have no experimental evidence that proves directly that in water and acetone the anion of silver nitrate is more "hydrated" than the cation, yet, by analogy with the alcohol and water mixtures, we should expect this to be the case. A study of Fig. XI. will show that in these mixtures there is at first a decrease, which is more marked at the lower temperature, in the relative velocity of the anion as alcohol is added to the solution. The turning point in the direction of the curve, however, is already reached in the mixture containing only 25 per cent of acetone. This is what we should expect if the effect of pure acetone on the relative ionic velocities of the anion and cation is taken into account. Although we have been unable to determine the transport numbers in pure acetone, all measurements made with mixtures containing increasing quantities of it tend to show that in the pure solvent the relative velocity of the anion is greater even than in pure ethyl alcohol. It is not surprising, therefore, that the addition of more than 25 per cent to an aqueous solution should entirely offset the effect of decreasing hydration and produce an increase in the relative velocity of the anion.

The results for mixtures of methyl alcohol and acetone are of the same nature. As with mixtures of water and acetone, we have no direct evidence that one ion carries more of one of the constituents of the solvent mixture than the ion of opposite charge. But a study of Fig. XII. makes it seem probable that the anion carries methyl alcohol with itself. At 0°, as the proportion of acetone is increased, the value for the transport number of the anion passes through a pronounced mini-

mum in the 25 per cent mixture. At 25° there is no actual minimum, but up to the 25 per cent mixture there is practically no increase in the relative velocity of the anion. It is interesting to note that in these mixtures, although the transport number of the anion is less at 0° than at 25°, the influence of the solvent is, as usual, more pronounced at the lower temperature.

The data for mixtures of ethyl alcohol and acetone (Table LXIX.) are too fragmentary to make any generalization possible, yet they show that the relative velocity of the anion passes through a minimum in the mixture containing 25 per cent of acetone.

The striking parallelism exhibited by calcium and silver nitrates, when their conductivity phenomena in binary mixtures of acetone with water and methyl and ethyl alcohols are compared, is very interesting in view of certain relations observed by Jones and Bingham between the conductivities of potassium iodide, calcium nitrate and lithium nitrate, and the migration velocities of the cations of these salts. Our conductivity measurements confirm the conclusions reached by them, but as it has no direct bearing on this investigation, reference only is made to their work.[1]

Summary.

1. We have measured the conductivity of silver nitrate in acetone, and in binary mixtures of this solvent with water, methyl alcohol and ethyl alcohol. The results were of the same general nature as those obtained by Jones and Bingham for calcium nitrate.

2. The transport number of the anion of silver nitrate in binary mixtures of water, methyl alcohol, ethyl alcohol and acetone has been determined at two temperatures, 0° and 25°.

3. That increase in temperature, in general, increases the velocity of the slower ion has been confirmed. Solutions in mixtures of methyl alcohol with acetone, in pure methyl alcohol and in a 75 per cent mixture of methyl alcohol with water are exceptions.

[1] THIS JOURNAL, 34, 481 (1905).

4. It has been shown that the nature of the solvent very materially affects relative migration velocities. That this is due to varying degrees of combination of the solvent with one of the ions, as compared with the ion of opposite charge, is very probable.

PHYSICAL CHEMICAL LABORATORY,
JOHNS HOPKINS UNIVERSITY,
May, 1906.

Contribution from the Kent Chemical Laboratory of the University of Chicago.

ON THE CONSTITUTION OF THE ACETYLIDENE COMPOUNDS.

BY JAMES WRIGHT LAWRIE.

It is now 9 years since Nef came to the conclusion that certain halogen substitution products of the hydrocarbon, C_2H_2, were acetylidene compounds,[1] containing bivalent carbon. At that time it seemed probable that 2 series of halogen substitution products of C_2H_2 might exist; namely, the monohalogen acetylenes, XC ⋮ CH, and the corresponding halogen substituted acetylidenes, HCX : C, as well as the halogen disubstituted acetylenes, XC ⋮ CX, and the isomeric dihalogenated acetylidenes, X_2C : C. This has since been found not to be the case and it is now certain that the so-called mono- and dihalogenated acetylenes are *all* acetylidene compounds; furthermore, tautomeric conceptions cannot be applied here to explain the non-existence of their isomers—the real mono- and dihalogen substituted acetylenes.

The sweet smelling, harmless, monoiodacetylene of Paterno and Peratoner[2] does not exist, but has been shown by Peratoner and Spallino[3] to consist of a mixture of acetylene, vinyl chloride, ethylidene chloride and acetylene diiodide. The isomeric, poisonous substance described by Baeyer as iodacetylene[4] has been proved by Nef[5] to be diiodacetylidene. On the other hand, halogen substitution products of monoalkylated and monoarylated acetylenes as CH_3C ⋮ CI and C_6H_5C ⋮ CX

[1] Ann. Chem. (Liebig), **298**, 332 (1897).
[2] Gazz. chim. ital., **19**, 584.
[3] Ber. d. chem. Ges., **34**, 2718–20 (1901).
[4] *Ibid.*, **18**, 2274.
[5] Ann. Chem. (Liebig), **308**, 325–6 (1899).

($X = Cl$, Br, or I) have since been isolated by Nef;[1] their properties—sweet smelling, harmless—are in marked contrast to those of the acetylidene compounds which are all very poisonous and spontaneously combustible substances.

Nef's proof of the constitution of the acetylidene compounds is as follows:[2] The perhalogen ethylenes, $X_2C : CX_2$, lose, on treatment with alcoholic potassium hydroxide, one pair of halogen atoms, giving, in the case where X represents iodine, C_2I_2, and where X is bromine the corresponding alcoholate of C_2Br_2, namely, ethyl dibromvinyl ether, $C_2Br_2HOC_2H_5$, whose constitution, as was sharply proved by him, must be represented by the formula $Br_2C : CHOC_2H_5$. Nef, therefore, assumed that in the latter case dibromacetylidene must first be formed, but being too reactive, it at once absorbed the alcohol present, giving the unsymmetrical ethyl dibromvinyl ether; he, in fact, made many attempts to isolate the intermediate product, dibromacetylidene, but without success. Quite recently Lemoult has isolated this compound by the action of alcoholic potassium hydroxide on tribromethylene, $Br_2C : CHBr$, in the cold; he, however, considers it to be dibromacetylene.[3] Lemoult obtained from it an addition product with iodine, which, from its properties, melting point 95°, etc., is obviously identical with Nef's unsymmetrical dibromdiiodethylene, $I_2C : CBr_2$.[4] It was, therefore, evident that the constitution of all the halogen substituted acetylidenes could now be determined with absolute precision and, consequently, I began experiments in this direction at the suggestion and under the guidance of Dr. Nef. Our expectations have been realized; my results confirm in every detail the conclusions previously reached by Nef. Briefly stated, the evidence now establishing the constitution of the acetylidene compounds is the following: Dibromacetylidene gives, with hydrogen iodide at ordinary temperatures, the addition product dibromiodethylene, C_2Br_2HI, as a heavy oil, boiling at 91° (15 mm.). This product must possess the constitution represented by the formula $Br_2C : CHI$,

[1] Ann. Chem. (Liebig), **308**, 292–323.
[2] *Ibid.*, **298**, 336, 340–1.
[3] Bull. Soc. Chim. de Paris, **43**, 193. Cf. Compt. rend.; **136**, 1333; **137**, 55; **139**, 131.
[4] Ann. Chem. (Liebig), **298**, 353.

first, because it can be converted smoothly, by oxidation with fuming nitric acid at —10°, into iodine and dibromacetic acid,

$$2Br_2C : CHI + 3O + H_2O \rightarrow 2Br_2CHCOOH + I_2;$$

second, because it gives, on treatment with alcoholic sodium phenolate, a large yield of unsymmetrical phenyl dibromvinyl ether, according to the equation

$$Br_2C : CHI \rightleftharpoons Br_2C : C< + HI + NaOC_6H_5 \rightarrow$$
$$Br_2C : C< + HOC_6H_5 + NaI \rightarrow Br_2C : CHOC_6H_5 + NaI.$$

That the two bromine atoms in phenyl dibromvinyl ether are bound to one and the same carbon atom is certain, because this compound can be converted, almost quantitatively, by fuming nitric acid, at —10°, into isomeric nitrated phenyl dibromacetates, $Br_2CHCOOC_6H_3(NO_2)_2$, which give, on treatment with dilute or concentrated cold, aqueous ammonia, the isomeric dinitrophenols and dibromacetamide. From this, it follows definitely that dibromacetylidene has its two bromine atoms bound to one and the same carbon atom. Since dibromacetylidene diiodide, $Br_2C : CI_2$, and diiodacetylidene dibromide are proved to be identical as regards their chemical and physical properties, it follows, further, that diiodacetylidene must possess the constitution represented by the formula $I_2C : C$. Finally, since Nef has shown that bromacetylidene gives, with iodine, the addition product,[1] $BrCH : CI_2$, which, on treatment with alcoholic potassium hydroxide or potassium acetate, gives potassium bromide and diiodacetylidene, the conclusion is unavoidable that in bromacetylidene the halogen and hydrogen atoms are both bound to the same carbon atom, as represented by BrCH : C. The so-called chloracetylene of Wallach[2] must, therefore, also be represented by the acetylidene formula, ClCH : C, since this compound possesses chemical and physical properties which, in every detail, resemble most strikingly those of the analogous bromacetylidene. The known mono- and dihalogen substitution products of acetylene, therefore, all belong to the acetylidene series ; the corresponding derivatives

[1] Ann. Chem. (Liebig), **298**, 359.
[2] *Ibid.*, **300**, 88

of acetylene are unknown and it is exceedingly improbable that any such compounds can be isolated.

EXPERIMENTAL PART.

Properties of Dibromacetylidene.

All the dibromacetylidene used in my experiments was prepared according to Lemoult's later directions from tribromethylene in cold alcoholic solution in the presence of 1.5 molecules of potassium hydroxide. Dibromacetylidene boils at 76° and has sp. gr. about 2. Lemoult states in his first paper in the *Comptes rendus* that he obtained at least an 80 per cent yield, but he never succeeded in obtaining over 15 per cent of the pure product in his later work.[1] He was, finally, compelled to stop work on the subject because of many violent explosions. I also had one very serious explosion with dibromacetylidene and found, moreover, that it possesses an intensely nauseating odor, resembling that of diiodacetylidene and of the isocyanides. The substance is intensely poisonous, causes headaches, indigestion and feelings of exhaustion, with most noticeable loss of memory. Terrific explosions may take place without the slightest warning when handling the substance in an atmosphere of carbon dioxide or of nitrogen; these are, undoubtedly, due to the presence of a trace of oxygen, which causes the dibromacetylidene to burn locally with violence; a sudden dissociation of the main product into bromine and diatomic carbon then results,

$$Br_2C : C \rightleftarrows C : C + Br_2.$$

The explosions in this case, as well as in that of acetylene and its heavy metal salts and the other halogenated acetylidenes must, therefore, all be attributed to the tremendous energy of the diatomic carbon.[2] It should be emphasized in this connection that Nef, in all his experiments with bromacetylidene, never had an explosion, whereas Wallach found that chloracetylidene often exploded spontaneously, in an inert atmosphere. It is, therefore, certain that all these substances can

[1] Bull. Soc. Chim. de Paris, 43, 193.
[2] Nef: Ann. Chem. (Liebig), 298, 348.

be handled without danger, but rigid precautions must be taken to ensure the absence of all traces of oxygen; it requires, furthermore, the constant presence of at least two persons to handle the substances properly. In view of all these experiences, I finally carried out most of my experiments with crude dibromacetylidene, and took special precautions never to inhale its vapors; the pure substance was handled only when absolutely necessary.

Crude dibromacetylidene, containing unchanged tribromethylene and traces of ethyl bromacetate and unsymmetrical ethyl dibromvinyl ether, can be prepared with the greatest ease, in the following manner: Twenty-six and one-half grams of tribromethylene and 1.5 molecules of potassium hydroxide (10.5 grams of 82 per cent KOH) are mixed in cold, alcoholic solution in a nitrogen atmosphere, care being taken to use the least possible amount of 95 per cent spirit, 35–50 grams, and the mixture is kept cool by running water, or by shaking in a large pail of ice-water. The operation is best carried out in a separatory funnel of about one liter capacity, provided above with a two-holed rubber stopper in which are inserted a small dropping funnel and a bent glass stop-cock. After 2 hours 400–500 cc. of cold water, freed from air, is slowly added and the larger part of the dibromacetylidene, besides other products, separates out at the bottom as a heavy oil, 12.1 grams, which can then be drawn off below and collected in a proper receiver, filled with dry carbon dioxide or nitrogen; this oil can at once be distilled from the receiver, the only product which passes over when the temperature of the surrounding oil-bath is 100°–120° being dibromacetylidene. For most purposes, however, the crude oil, 12.1 grams, containing about 7 grams of dibromacetylidene was used directly. In this operation about one-third of the dibromacetylidene formed in the reaction is lost because it remains dissolved in the supernatant, aqueous-alcoholic solution. It was found that 2 hours' standing of the reaction mixture gave the best results, since by longer standing the dibromacetylidene is slowly converted into monobromacetylidene. It was easily possible to establish this point, as well as the nature of the other products formed in the reaction,

in the following manner: The crude oil separated off by addition of much water, or the original reaction mixture, after standing from 2 to 24 hours, was treated, in alcoholic solution, with an excess of finely powdered iodine (25 grams) and allowed to stand for 2 days at the ordinary temperature. In this way all the mono- and dibromacetylidene present are converted into their corresponding iodides, $BrCH : CI_2$ and $Br_2C : CI_2$; the former is a liquid, boiling at 115° (15 mm.) and the latter a crystalline solid which is left behind in the distilling flask after all the other products present have been distilled over under reduced pressure. The method of procedure, therefore, was to add much water to the iodine mixture and extract well with ether; the ethereal solution was then washed with aqueous sodium hydroxide, to get rid of the iodine and the oils left, after drying with calcium chloride and removing the ether, were distilled under reduced pressure. Ethyl bromacetate, tribromethylene and unsymmetrical dibromvinyl ethyl ether boil at 159°, 163° and 170° under ordinary pressure; they are, therefore, found in the lower boiling fractions and are then separated and identified according to Nef's directions;[1] the higher boiling fraction, 100°–115° (15 mm.), is found to consist chiefly of bromacetylidene diiodide, which is readily identified by treatment with alcoholic potassium hydroxide and subsequent conversion of the crude diiodacetylidene formed[2] into periodethylene (m. p. 184°). The presence of these substances in the reaction products of alcoholic potassium hydroxide on tribromethylene is self-evident from the work of Nef. It was noticed, in this way, that the yield of dibromacetylidene diminishes, while that of bromacetylidene increases if the original alcoholic potassium hydroxide solutions of tribromethylene are allowed to stand longer than 2 hours in the cold. This proves that dibromacetylidene is slowly transformed, on standing in cold, slightly alkaline solution, or more rapidly on heating into bromacetylidene, and this explains why Nef failed to isolate dibromacetylidene in his experiments with tribromethylene and alcoholic potassium hydroxide.

[1] Ann. Chem. (Liebig), 298, 334–36.
[2] *Ibid.*, 298, 359.

In an experiment where 26.5 grams of tribromethylene, 50 parts of alcohol and 10.5 grams of 82 per cent potassium hydroxide were used, the reaction mixture, after 2 hours' standing in the cold, gave, on treatment with 25 grams of iodine, 24.6 grams of pure dibromdiiodethylene, melting at 95°; this proves that 56.2 per cent of the theoretical amount of dibromacetylidene is formed under these conditions. When I used the same amounts of the reagents, but allowed the mixture to stand 24 hours, at room temperature, before adding iodine, only 18.1 grams of dibromdiiodethylene, 41.1 per cent of the theory and 7.1 grams of crude diiodbromethylene, b. p. 100°–115° (15 mm.) were obtained, whereas the amouut of the latter substance isolated in the first experiment was only 3 grams. The 7.1 grams of crude bromacetylidene diiodide obtained in the second experiment gave, on treatment with 1.3 grams of potassium hydroxide in 10 cc. of alcohol, and subsequent standing for 12 hours in the cold, potassium bromide and an oil, which, with 7 grams of iodine, in ethereal solution, gave, finally, 2.8 grams of pure periodethylene, melting at 184°. In addition, the presence of much unchanged tribromethylene and traces of unsymmetrical dibromvinyl ethyl ether, $Br_2C:CHOC_2H_5$, was established in the lower boiling fraction, 50°–100° (20 mm.). In order to determine how much dibromacetylidene is present in the crude oil separated by the addition of much water, the following experiment was carried out: A mixture of 26.5 grams of tribromethylene, 35 grams of 95 per cent alcohol and 10.5 grams (82 per cent) potassium hydroxide were allowed to stand 2 hours, in the cold, and then 400 cc. of water were added. The oil which separated was allowed to run directly into 200 cc. of ether and 25 grams of iodine, etc. Only 16.9 grams of dibromdiiodethylene, 38.6 per cent of theory, were obtained, which proves that about one-third of the dibromacetylidene formed in the reaction must have remained in the aqueous-alcoholic solution. No bromacetylidene diiodide was obtained in this experiment; it is evident that only traces of bromacetylidene can be present in the oil separated by the addition of water, as the small amount of bromacetylidene formed in the reaction must practically all re-

main in the aqueous-alcoholic solution. The crude oil, 12.1 grams, which separates off by addition of water, therefore contains about 7 grams of dibromacetylidene; the other product present, as was often established by special experiments, is chiefly tribromethylene containing traces of ethyl bromacetate and unsymmetrical dibromvinyl ethyl ether.

Dibromiodethylene,

$Br_2C : CHI.$

All attempts to add alcohol, phenol, acetic, formic and trichloracetic acid to dibromacetylidene, either at ordinary temperatures, or in sealed tubes at 100°, were attended with negative results; the addition of alcohol or phenol to this substance only takes place when it is set free in a *nascent condition* from tribromethylene by potassium hydroxide, sodium ethylate, or sodium phenolate, according to the equation

$$Br_2C : CHBr \rightleftharpoons Br_2C : C< + HBr.$$

The salt present first removes one of the products of dissociation, the hydrogen bromide, and the active or nascent dibromacetylidene, before it can transform itself into inactive dibromacetylidene, $Br_2C : C]$, may absorb, in part or entirely, according to the speed of the reaction, the dissociated alcohol, $H—OC_2H_5$, or phenol, $H—OC_6H_5$, present, giving, thus, the addition products, $Br_2C : CHOC_2H_5$ and $Br_2C : CHOC_6H_5$. Nef has repeatedly made similar observations in his more recent work on the alkyl halides, alcohols, etc.[1] The dibromacetylidene, as such, contains, at 20°–100°, too small a proportion of active particles,[2]

$$Br_2C : C] \rightleftharpoons Br_2C : C<,$$

to be able to absorb readily such reagents as alcohol, water, ammonia, phenol, or acetic acid. It, however, absorbs with the greatest of ease such reagents as bromine, iodine, hydrobromic acid and hydrogen iodide. The addition product with hydrogen iodide is of especial interest, as it is possible, by

[1] Ann. Chem. (Liebig), **309**, 126–189; **310**, 316–335; **318**, 137–230; **335**, 191–333.
[2] Nef: J. Am. Chem. Soc., **26**, 1555, 1563.

means of it, to prove that the 2 bromine atoms in dibromacetylidene are bound to the same carbon atom.

Crude dibromacetylidene, from 26.5 grams of tribromethylene,[1] is added, cooling with ice-water, to 40 grams of aqueous hydriodic acid, sp. gr. 1.96, which was first freed from all possible traces of free iodine by means of 2 grams of red phosphorus. There was a noticeable rise in temperature and the mixture was finally allowed to stand in a carbon dioxide atmosphere for 2 hours at the ordinary temperature; water was then added and the oil extracted with ether, washed with sodium hydroxide and dried with calcium chloride. On fractionation, under reduced pressure, 10 grams of dibromiodethylene were obtained. It is a sweet smelling oil, boiling at 91° (15 mm.) and having sp. gr. 2.952 at 24° (Westphal). In addition, 3 grams of dibromdiiodethylene, melting at 95°, were isolated from the residue left in the distilling flask. If no precaution is taken to free the hydrogen iodide used from iodine, practically only dibromdiiodethylene is obtained as the reaction product. Analysis:

0.2782 gram substance gave 0.5528 gram 2AgBr,AgI by the Carius method, and subsequent electrolysis of the 2AgBr,AgI, in potassium cyanide solution, gave 0.2985 gram, or 53.9 per cent of silver instead of the theoretical 53.2 per cent Ag.

0.7031 gram substance gave 0.1972 gram CO_2 and 0.0225 gram H_2O.

	Calculated for C_2Br_2HI.	Found.
C	7.68	7.61
H	0.32	0.35
Br_2I	92.0	93.3

I attribute the high percentage of halogen found to the presence of mechanically enclosed silver nitrate.

A mixture of 10 grams dibromiodethylene, in 17 grams of

[1] A special experiment with 12.1 grams pure tribromethylene, 40 grams hydriodic acid, sp. gr. 1.96, and 2 grams of phosphorus proved that, after standing 2 hours at 0°, under the same conditions, therefore, as in the experiment given above, this substance remains entirely unchanged; for 10 grams tribromethylene, boiling at 73° (33 mm.), were recovered on working up the mixture in the usual manner. Furthermore, iodine, in ethereal solution, does not act on tribromethylene after standing for three weeks at the ordinary temperature.

alcohol containing 3.5 grams of potassium hydroxide, was allowed to stand at 0° for 2 hours; 12 grams of powdered iodine were then added and, after 12 hours' standing and working up as in the previous cases, 6.4 grams of dibromdiiodethylene, m. p. 95°, were obtained. This proves that a fair amount of dibromacetylidene must have been formed in the reaction.

On the Conversion of Dibromiodethylene into Dibromacetic Acid.

As mentioned in the introduction, dibromiodethylene, 10 grams, is transformed smoothly by 2 parts of fuming nitric acid, at —10°, into dibromacetic acid. The oil, which is added drop by drop to the acid, dissolves and iodine at once separates out; there is a noticeable rise of temperature which must be properly controlled by shaking. The mixture was finally allowed to stand a short time surrounded by ice-water and was then poured on ice, extracted 5 times with ether and the ethereal solution was freed from acids by extracting with dilute sodium carbonate solution. The alkaline solutions then gave, on acidifying, extracting 5 times with ether, etc., 5.7 grams of dibromacetic acid, b. p. 107°–110° (30 mm.), m. p. 47°–48°. The substance was further identified by dissolving 3.5 grams in 12 cc. of absolute alcohol and heating for 3 hours at 100°–102°, in the presence of concentrated sulphuric acid; 3.6 grams of crude ethyl dibromacetate were obtained which, on treatment with 30 cc. of 10 per cent ammonia, at —5°, gave 1.9 grams of pure dibromacetamide, m. p. 156°, which was analyzed for halogen.

0.2105 gram substance gave 0.3629 gram AgBr (Carius).

	Calculated for $C_2H_3ONBr_2$.	Found.
Br	73.73	73.35

An entirely analogous experiment was carried out with 10 grams of tribromethylene and 20 grams of fuming nitric acid, but it was found necessary to heat the mixture to 100° in order to dissolve all the halogen compound. On working up the reaction products as above, 6 grams of dibromacetic acid, m. p. 40°, were obtained; 4.8 grams of this, heated with 10 grams of absolute alcohol and 2 grams of concentrated sul-

phuric acid, for 3 hours, at 105°, gave 4.5 grams of crude ethyl dibromacetate, from which, by means of 10 per cent ammonia, at —10°, 2.5 grams of pure dibromacetamide, m. p. 156°, were obtained. In this case a fair amount of neutral products was also isolated; these yielded 2.1 grams, at 108°–110° (15 mm.) and, on cooling, 0.7 gram of perbromethylene, m. p. 53°–54°, separated out. The oil remaining was tribromnitroethylene, $Br_2C : CBrNO_2$, obtained by Scholl and Brenneisen,[1] by the action of nitric acid on tribromethylene.

It is obvious that the conversion of tribromethylene and of dibromiodethylene into dibromacetic acid by nitric acid is due to a combustion of the dibromacetylidene, which is a common dissociation product in both cases:

$$Br_2C : CHBr \rightleftharpoons Br_2C : C< + HBr \quad \text{and}$$

$$Br_2C : CHI \rightleftharpoons Br_2C{:}C< + HI.$$

The dibromacetylidene oxidizes first to dibromacetylidene oxide, $Br_2C : CO$, which then absorbs water or nitric acid, giving, finally, dibromacetic acid. This is shown also by the fact that tribromethylene, as well as tetrabromethylene, take up oxygen directly at low temperatures (50°), giving dibromacetyl bromide, $Br_2CHCOBr$, and tribromacetyl bromide, Br_3CCOBr, respectively. It is clear that the common dissociation product, $Br_2C : C$, first takes up one atom of oxygen and the oxide formed then unites at once with the other dissociation product present, HBr or Br_2, to give the substances actually obtained.[2] It is clear that the experiments of Henry on trichlorvinyl ethyl ether,[3] as well as those of Swarts on perhalogenated ethylenes and on dibromfluorethylene,[4] must be interpreted in a similar manner.[5] In repeating an

[1] Ber. d. chem. Ges., **31**, 651. Cf. Biltz and Kedesdy: *Ibid.*, **33**, 2191.

[2] Cf. Nef: Ann. Chem. (Liebig), **298**, 365. Demole: Ber. d. chem. Ges., **11**, 315; **12**, 2245. Bull. Soc. Chim., **34**, 201. *Vide* also recent experiments of Bacon and Goldthwaite from this laboratory. THIS JOURNAL, **30**, 455; **33**, 75.

[3] Ber. d. chem. Ges., **12**, 1838.

[4] Bul. Acad. Belg. [3], **35**, 849; **36**, 532. Centrabl., 1898, II., 702; 1899, I., 588.

[5] Dr. Nef informs me that he now believes that the spontaneous combustibility of zinc ethyl (Cf. Ann. Chem. (Liebig), **298**, 331, foot-note) undoubtedly depends upon the fact that ethylidene dissociation exists at ordinary temperatures according to

$$Zn(C_2H_5)_2 \rightleftharpoons ZnH_2 + 2CH_3CH=$$

(Cf. Ann. Chem. (Liebig), **309**, 165; **310**, 317–335; **318**, 1–55). The remarkable behavior of zinc ethyl towards chloroform, bromoform and carbon tetrachloride (Cf. Beilstein; working with Rieth and Alexeyeff. Ann. Chem. (Liebig), **124**, 245 and Jahres. d. Chem., 1864, 470) may also be very simply explained on this basis.

experiment of Demole with 10 grams of tribromethylene and dry oxygen, in a bath kept at 140°, I have found that besides 4.1 grams dibromacetyl bromide, b. p. 57°–80° (11 mm.), 5.2 grams of oil boiling at 119° (11 mm.) are obtained; the latter solidified, in great part, on cooling, and was proved to be perbromethylene. The oil left, in all 7 grams, gave, on treatment with 30 cc. of 10 per cent ammonia, 2.4 grams of pure dibromacetamide, m. p. 156°. It is, therefore, evident that the conversion into dibromacetyl bromide is not quantitative. From the results obtained in the burning of dibromacetylidene itself (see below) it is exceedingly probable that some of the dibromacetylidene oxide first formed unites further with oxygen, giving bromine and carbon monoxide; the bromine must then naturally give with the tribromethylene, or its product of dissociation, $Br_2C:C$, the perbromethylene which I obtained in such large quantity in my experiment. Finally, brief mention should be made of an attempt to oxidize dibromiodethylene, $Br_2C:CHI$, in the presence of dry oxygen, in a flask placed in a bath at 140°. It is obvious, from the theory of the reaction, that dibromacetylidene oxide and hydrogen iodide must first result, the hydriodic acid must then at once react with the oxygen present to give free iodine and detonating gas. This was proved in a most frightful manner by the explosion which took place when I, by inadvertence, applied the splinter test for oxygen to the gaseous mixture.

On the Oxidation of Dibromacetylidene in Dry Oxygen.

Nef[1] has shown that diiodacetylidene and bromacetylidene burn in the presence of oxygen to give chiefly carbon monoxide, periodethylene, or ethylene bromide, according to the following equations:

$$2I_2C:C + 2O \rightarrow I_2C:CO + I_2C:C + O \rightarrow OC:CO + I_2 + C:CI_2 \rightarrow I_2C:CI_2 + 2CO;$$

and

[1] Ann. Chem. (Liebig), 298, 345, 358.

$$2BrHC:C + 2O \rightarrow$$
$$BrHC:CO + BrHC:C + O \rightarrow$$
$$C:CO + HBr + BrHC:C + O \rightarrow$$
$$OC:CO + BrHC:CHBr \rightarrow$$
$$BrHC:CHBr + 2CO.$$

It was, therefore, to be expected that dibromacetylidene would behave in a similar manner, giving 2 molecules of carbon monoxide and perbromethylene. This was found to be the case; about 78.4 per cent of the oxidation takes place in this way, but some very interesting side reactions, which are theoretically self-evident, also occur. Lemoult[1] has studied the behavior of dibromacetylidene under water, or dissolved in alcohol, towards oxygen and finds that oxalic acid is a reaction product; he assumes that oxalyl bromide is first formed, according to the equation:

$$BrC:CBr + 2O \rightarrow BrCOCBrO,$$

etc., but he gives no quantitative data and states that other products containing halogen are also formed. In my first experiments I tried the action of dry oxygen on dibromacetylidene dissolved in moist or in absolute ether, but found that, under these conditions, practically no oxidation takes place as the substance was recovered unchanged; the best condition for studying the behavior of this substance towards oxygen was, finally, found to be in the presence of absolute alcohol. Because of their interest, I shall first give, however, a brief summary of my experiments with dibromacetylidene and oxygen, in the presence of dry and moist ether.

Crude dibromacetylidene, made from 53 grams of tribromethylene, was separated by the addition of water, drawn off into a receiver filled with dry carbon dioxide and then heated[2] in an oil-bath up to 100°–120°. About 11 grams of pure dibromacetylidene, b. p. 76°, distilled over and was collected in a flask containing 70 cc. of ether and 5 cc. of water. The flask was now connected with a small gasometer filled with water,

[1] *Loc. cit.*

[2] In an experiment in which I attempted to repeat this operation, the dibromacetylidene exploded with terrific violence the moment the oil struck the bottom of the receiver. I imagine traces of air must have been left in the receiver.

with three intervening wash bottles containing 30 per cent potassium hydroxide to absorb any carbon dioxide formed in the reaction. Dry oxygen was then allowed to bubble slowly through the ethereal solution of dibromacetylidene, at the rate of 700 cc. per hour, for 6 hours; the gaseous products naturally collected in the small gasometer. No trace of carbon monoxide was formed, as determined by absorbing the gases first by pyrogallol and then by ammoniacal cuprous chloride. The ether solution was now distilled over on a water-bath into a receiver containing iodine; 16.3 grams of dibromacetylidene diiodide, m. p. 95°, were obtained on working up in the usual manner, which shows that the dibromacetylidene had not been acted upon. An experiment, using absolute ether and crude dibromacetylidene gave an entirely similar result. It was now observed that ethereal solutions of dibromacetylidene could be poured from flask to flask and exposed to the air without the slightest fuming; one can even distil off most of the ether by means of a Glinsky apparatus and the oil left, which still contain small amounts of ether, burns only very slowly at the ordinary temperature. It can be poured into a distilling flask and then be fractionated under reduced pressure; on opening the Brühl apparatus the dibromacetylidene fraction, 37° (60 mm.), burns with great violence at once in the air; there is no explosion, however, but the Brühl apparatus becomes entirely covered with soot. A special examination of the residue, about 12 grams, after the 11 grams of dibromacetylidene, mentioned above, from 53 grams of tribromethylene had been removed by heating in an oil-bath at 100°–120°, gave the following result: Two fractions, besides 5 grams of non-volatile tar, were obtained on distillation under reduced pressure; the lower fraction, 0.8 gram, b. p. 67°–75° (17 mm.), possessed the sharp odor of ethyl bromacetate; the other boiled at 108°–110° (12 mm.) and solidified at once on cooling, giving 4 grams of crystals of perbromethylene[1], m. p. 55°–56°. The lower boiling fraction gave, on treatment with ammonia, a trace of bromacetamide; the oil left had now lost its

[1] No perbromethylene, C_2Br_4, is present in crude dibromacetylidene; its presence here is probably due to a dissociation of C_4Br_2 into Br_2 and C_2 with subsequent absorption of Br_2 by C_4Br_2 to form C_2Br_4.

pungent odor and gave, on treatment with concentrated nitric acid in the cold, a neutral, oily mixture which, on treatment with ammonia, gave a very small amount of crystals of dibromacetamide, m. p. 156°, thus proving the presence of asymmetrical dibromvinyl ether. Finally, there was left an insoluble, neutral, sweet smelling oil, possessing all the properties of tribromethylene (this was the main product).

On the Oxidation of Dibromacetylidene in the Presence of Alcohol.

Crude dibromacetylidene, from 53 grams of tribromethylene and containing, therefore, according to the quantitative conversion into iodide, given above, 14 grams of dibromacetylidene was run into a flask, filled with carbon dioxide, containing 50 grams of absolute alcohol; the flask was connected with the usual train of 3 washing bottles containing 30 per cent potassium hydroxide and, finally, with the gasometer filled with water. Dry oxygen was then passed through the mixture, which was cooled with ice-water and shaken continually at first, at the rate of 1 liter per hour for 3.5 hours, during which time the temperature of the surrounding water was allowed to go up to 20°. There was a slight fuming noticed at the beginning and at the end no trace of unchanged dibromacetylidene could be detected in the alcoholic solution. The analysis of the gaseous mixture which had collected in the gasometer gave, at 20° and 755 mm., 800 cc. of carbon monoxide from a total volume of 2550 cc. The excess of oxygen present in 100 cc. was first absorbed by pyrogallol, and the carbon monoxide left was then determined by ammoniacal cuprous chloride. The amount of carbon monoxide which can be formed, according to the equations given above, from 14 grams of dibromacetylidene is 1.7 liters. Hence, about 47 per cent of the theoretical amount was actually obtained ; there is no doubt that a large proportion of the nascent carbon monoxide produced by the dissociation of the dimolecular product, $OC : CO \rightleftharpoons 2OC<$ first formed in the oxidation unites at once with the oxygen present to give carbon dioxide. Nef observed that much carbon dioxide, as well as carbon monoxide, is formed in the burning of bromacetylidene in aqueous

solution, by oxygen.[1] In order, therefore, to have an exact determination of the percentage of oxidation of dibromacetylidene which takes place according to the equation,

$$2C_2Br_2 + O_2 \rightarrow C_2Br_4 + 2CO,$$

it is obviously necessary to determine also the proportion of the carbon monoxide which has been oxidized to carbon dioxide. This would easily have been possible by means of a separate quantitative experiment in a nitrogen atmosphere, but as the large amount of perbromethylene obtained at the end of the oxidation, as well as the other data, also establish the point pretty accurately, proving that about 78.4 per cent proceeds according to the equation given, an exact determination was deemed unnecessary. An investigation of the products present in the alcoholic solution after oxidation was carried out as follows: Much water was added, and the oils separating out were extracted with ether; the ethereal solution was then washed well with water. The water solution contained a large amount of hydrobromic acid and traces of oxalic acid. The ether was removed, after drying with calcium chloride, by means of a Glinsky apparatus, and the oils left behind were fractionated (16 mm.). The following fractions were obtained: I. 8.9 grams, b. p. 55°–73; II. 8.5 grams, b. p. 81°–90°; III. 2.3 grams, b. p. 95°–110°, which solidified at once on cooling and consisted of practically pure perbromethylene. Fractions I. and II. were treated separately, at —10°, with 25 cc. and 45 cc. of 10 per cent ammonia; 0.15 and 0.8 gram of oxamide, respectively, with all its characteristic properties, were obtained.

0.5551 gram substance gave 0.2134 gram NH_3 (Kjeldahl).

	Calculated for $(CONH_2)_2$.	Found.
N	31.81	31.68

On spontaneous evaporation of the aqueous ammoniacal solutions used in the experiments just mentioned, and subsequent digestion of the salt residue with benzene, 1 gram of pure dibromacetamide, m. p. 156°, was obtained. The oils

[1] Ann. Chem. (Liebig), 298, 358.

left insoluble and unaffected by the treatment with ammonia, fractions I. and II., were combined and, on distillation (15 mm.), 7.3 grams of oil, b. p. 65°–75°, or b. p. 163°–167°, under ordinary pressure, were obtained which was proved to consist chiefly of tribromethylene containing small amounts of unsymmetrical dibromvinyl ethyl ether. In addition, 3.4 grams more of pure perbromethylene were obtained, which makes the total amount of pure perbromethylene, m. p. 55°–56°, 5.7 grams. On the assumption that the 14 grams of dibromacetylidene present at the beginning of the experiment burned completely according to the equation

$$2C_2Br_2 + O_2 \rightarrow C_2Br_4 + 2CO,$$

13.1 grams of perbromethylene must result. On the basis that 78.4 per cent of the reaction proceeds in this manner, 10.1 grams of perbromethylene must be formed; the amount actually obtained, 5.7 grams, is necessarily low because of the difficulty of separating sharply a mixture of tribromethylene and tetrabromethylene; furthermore, it is quite probable that a portion of the bromine set free also reacts with the large excess of alcohol present to give HBr, etc., and the hydrogen bromide formed may then, in part, give tribromethylene with the dibromacetylidene present. How are we, however, to explain the formation of the oxalic and dibromacetic acids? Obviously, as follows:

A. Dibromacetylidene, in taking up oxygen, first gives dibromacetylidene oxide, $Br_2C : CO$, and this substance must then, in part, 6.06 per cent by calculation from the above results, add 1 molecule of alcohol,

$$\begin{array}{l} Br_2CCO + H-OC_2H_5 \rightarrow Br_2CHCOOC_2H_5, \\ \quad | \quad | \end{array}$$

giving ethyl dibromacetate, which, on treatment with aqueous ammonia, then gives the dibromacetamide obtained in the experiment.

B. Dibromacetylidene oxide, however, being dissociated according to

$$Br_2C : CO \rightleftarrows Br_2 + >C : CO,$$

burns mainly to dimolecular carbon monoxide, OC : CO, which, in great part, spontaneously dissociates, giving monomolecular carbonic oxide, or unites with more oxygen to give carbon dioxide. The bromine which falls off from dibromacetylidene oxide is, in turn, mainly taken up by unchanged dibromacetylidene,

$$Br_2C : C + Br_2 \rightarrow CBr_2 : CBr_2,$$

giving tetrabromethylene ; a small percentage, 15.54 per cent by calculation from the data given above, of the bromine must, however, unite with the dimolecular carbon monoxide, OC : CO, to give oxalyl bromide,

$$Br_2 + OC : CO \rightarrow BrCOCOBr,$$

which at once gives, with the alcohol present, hydrogen bromide and ethyl oxalate ; the latter then gives, with ammonia, the oxamide obtained in the experiment.

The experiment described above shows, therefore, that dibromacetylidene, in alcoholic solution, unites with dry oxygen according to the following three equations :

I. Main reaction, 78.4 per cent, $2Br_2C_2 + O_2 \rightarrow Br_4C_2 + 2CO$ (including CO_2) ;

II. 15.54 per cent, $Br_2C_2 + O_2 \rightarrow BrCOCOBr$;

III. 6.06 per cent, $2Br_2C_2 + O_2 + 2H-OC_2H_5 \rightarrow 2Br_2CHCOOC_2H_5$.

Dibromacetylidene Diiodide and Diiodacetylidene Dibromide are Identical.

As mentioned above, Lemoult's dibromacetylidene diiodide was isolated in large amount because it was especially well adapted for the quantitative estimation of dibromacetylidene. The yellowish substance crystallizes from hot alcohol in large, flat, transparent needles and separates out almost completely. The identity with Nef's diiodacetylidene dibromide[1] was proved by a careful comparison of the two products as regards crystalline form, solubility, etc. Furthermore, the product analyzed by Nef in 1896, when mixed with an equal

[1] Ann. Chem. (Liebig), 298, 354.

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amount of dibromacetylidene diiodide, melted sharply at 95°, so that there can be no possible doubt as to the identity of the products. It follows, therefore, that diiodacetylidene must possess the constitution represented by the formula $I_2C:C$; and since bromacetylidene diiodide is converted smoothly, by means of alcoholic potassium hydroxide, sodium phenolate, or potassium acetate into bromide and diiodacetylidene,[1] the acetylidene formula is definitely established also in the case of the monohalogenated acetylidenes.

Phenyl dibromvinyl Ether, $Br_2C:CHOC_6H_5$, from Tribromethylene and from Unsymmetrical Dibromiodethylene.

Sabanejeff[2] found that on treating tribromethylene with alcoholic potassium phenolate, dibromvinyl phenyl ether, m. p. 38°, is formed in small quantity. Nef,[3] in repeating this experiment with alcoholic sodium phenolate, under definite conditions, obtained a very large yield of the substance and observed that it boils, without decomposition, at 143° (25 mm.). In repeating the experiment according to Nef's directions, I have obtained an 82 per cent yield of the pure product. The same substance is formed, furthermore, on treating the unsymmetrical dibromiodethylene, $Br_2C:CHI$, described above, with alcoholic sodium phenolate; this at once leads to the conclusion that the substance must possess the unsymmetrical formula, $Br_2C:CHOC_6H_5$, given to it by Nef. The correctness of this deduction was finally established beyond doubt by the quantitative conversion of dibromvinyl phenyl ether, by means of nitric acid, at −10°, into nitrated phenyl dibromacetate, etc.,

$$CHBr_2COOC_6H_3(NO_2)_2.$$

Finally, it is clear, as was pointed out by Nef in 1897, and as has since been confirmed in many instances by his work on the alkyl haloids,[4] that the interaction between tribromethylene or dibromiodethylene and alcoholic sodium or potassium phenolate must be interpreted as follows: The halogenated ethyl-

[1] Ann. Chem. (Liebig), **298**, 359.
[2] *Ibid.*, **216**, 283.
[3] *Ibid.*, **298**, 360 (foot-note).
[4] *Ibid.*, **298**, 359; **309**, 126; **318**, 1.

enes do not react as such, but because they are partially dissociated, at ordinary temperatures, according to the equation

$$Br_2C : CHX \rightleftharpoons Br_2C : C< + HX \ (X = Br \text{ or } I).$$

The metallic phenolate, therefore, is acted upon by the halogen acid present, giving metallic haloid and free phenol, $H—OC_6H_5$, which *may* or *may not*, depending *entirely* on the speed of the reaction, be added to the *other* dissociation product, $Br_2C : C<$, present, to give phenyl dibromvinyl ether, $Br_2C : CHOC_6H_5$. If the reaction proceeds too rapidly the active dibromacetylidene molecules, not finding enough dissociated phenol molecules present, go over, mainly, into the comparatively inert dibromacetylidene,

$$Br_2C : C< \rightarrow Br_2C : C],$$

which, as was proved by special experiments, when once formed, does not absorb phenol to any extent. The correctness of these conclusions was repeatedly confirmed in my experiments with tribromethylene and alcoholic sodium phenolate; thus, if one heats, rapidly, a mixture of molecular quantities of tribromethylene and sodium phenolate, much free dibromacetylidene and carbolic acid are formed and correspondingly smaller amounts of phenyl dibromvinyl ether; it is, in fact, impossible to prevent entirely the formation of dibromacetylidene in the experiment, but the following method gives always an 82 per cent yield of phenyl dibromvinyl ether.

An alcoholic solution containing sodium ethylate, from 4.3 grams of sodium, was slowly added, by means of a dropping funnel, to a solution containing 25 grams of tribromethylene, 19 grams of phenol and 25 cc. of alcohol. During the operation and for 12 hours afterwards the temperature was kept at 0°. Finally, the mixture was heated slowly to 100° and kept for 4 hours at that temperature to complete the reaction. On pouring into much water, extracting with ether, washing the ether solution with sodium hydroxide, then with water and drying with calcium chloride, 21.4 grams of phenyl dibromvinyl ether, a sweet smelling oil, boiling at 142° (25 mm.)

were obtained. The substance melts at 38°–39° and has sp. gr. 1.799 at 25° (Westphal).

0.4752 gram substance gave 0.6450 gram AgBr (Carius).

	Calculated for $C_2H_2OBr_2$.	Found.
Br	57.56	57.74

A fair yield of the same product was also obtained from dibromiodethylene by means of alcoholic sodium phenolate. Fifty cc. of an alcoholic solution containing sodium ethylate, from 4.3 grams of sodium, were slowly added to a cold solution of 28 grams of dibromiodethylene, b. p. 91° (15 mm.), 17 grams of phenol and 15 grams of alcohol; the mixture was allowed to stand at 0° for 17 hours and then gradually heated to 95° and kept at that temperature for 2 hours. On working up, as in the case just mentioned, 12.8 grams of phenyl dibromvinyl ether, b. p. 135°–140° (15 mm.), 52 per cent of the theoretical amount, were obtained. The oil solidified at once on cooling and the crystals, when mixed with an equal quantity of the corresponding substance from tribromethylene, melted unchanged at 38°–39°.

On the Conversion of Phenyl dibromvinyl Ether into Dibromacetamide.

Ten grams of phenyl dibromvinyl ether were added, drop by drop, to 30 cc. of fuming nitric acid at —10°; a hissing noise, with decided heat evolution, was noticed and the yellowish precipitate first formed dissolved subsequently on shaking. The mixture was left standing at room temperature for 2 days and then poured on ice. The oil which separated out was extracted with ether and washed with small amounts of water; after removing the ether it was mixed with 3 cc. of concentrated sulphuric acid and 20 cc. of absolute alcohol and kept for 3 hours[1] at 100°. On adding water, an oil, possessing a sharp odor and causing tears, was precipitated. This was treated with 75 cc. of 15 per cent aqueous ammonia, at —10°. The crystals which came out were collected and the residue obtained after the spontaneous evaporation of the ammoniacal solution was extracted with benzene. Thus a total of 4 grams

[1] E. Fischer: Ber. d. chem. Ges., 28, 3252.

of pure dibromacetamide, m. p. 155°–156°, were obtained which is 51.3 per cent of the amount theoretically possible.

0.1468 gram substance gave 0.2543 gram AgBr (Carius).

	Calculated for $C_2H_3Br_2NO$.	Found.
Br	73.73	73.71

On the Conversion of Phenyl dibromvinyl Ether into Bromacetic Acid.

Nef has shown that the analogous ethyl dibromvinyl ether, $Br_2C:CHOC_2H_5$, is converted, quantitatively, by fuming nitric acid into ethyl dibromacetate.[1] On treatment with alcoholic potassium hydroxide, on the other hand, this substance first gives ethyl bromacetate; consequently, Nef concluded that in this reaction, as well as in the analogous one with diiodacetylidene,[2] ethoxy halogen acetylene, $XC \vdots COC_2H_5$, must first be formed which, however, being too reactive, at once absorbs the alcohol or water present, giving ethyl halogen orthoacetate, $XCH_2C(OC_2H_5)_3$, or ethyl halogen acetate, $XCH_2COOC_2H_5$. Slimmer has since obtained similar results with alcoholic potassium hydroxide on the phenyl dibromvinyl ether of Sabanejeff and Nef.[3] I have, therefore, continued to study the behavior of phenyl dibromvinyl ether towards various reagents, especially in the hope of being able to obtain direct proof of the intermediate formation of bromphenoxyacetylene.

Phenyl dibromvinyl ether is remarkable on account of the ease with which it loses one of its halogen atoms. Thus it loses 1 molecule of hydrogen bromide on heating to 100° for a short time, in the presence of alcohol, water, or acetic acid; the other product formed, besides phenol, is invariably bromacetic acid or its ester. The only rational interpretation of these facts is the one given by Nef, namely, that phenyl dibromvinyl ether is dissociated according to the equation

$$Br_2C : CHOC_6H_5 \rightleftharpoons BrC \vdots COC_6H_5 + HBr,$$

[1] Ann. Chem. (Liebig), **298**, 335.
[2] *Ibid.*, **298**, 337, 349.
[3] Ber. d. chem. Ges., **36**, 289.

and that the bromphenoxyacetylene at once absorbs water, etc., giving phenol and bromacetic acid, thus :

$$BrCH_2C(OH)_2OC_6H_5 \rightarrow CH_2BrCOOH + HOC_6H_5.$$

In view of all this I made many attempts to isolate bromphenoxyacetylene, by treating phenyl dibromvinyl ether with alcoholic potassium hydroxide, powdered potassium hydroxide, aniline, quinoline, pyridine, etc., but always without success.

It should be pointed out here that the bromphenoxyacetylene mentioned by Sabanejeff[1] has been proved by Slimmer not to exist[2] and I have confirmed the results obtained by the latter.

Finally, I give a brief summary of my results obtained while studying the action of water, alcohol and acetic acid on phenyl dibromvinyl ether. It was hoped, at first, that in this way dibromacetaldehyde and phenol might be formed, according to the equation :

$$CBr_2:CHOC_6H_5 + H_2O \rightarrow CHBr_2CHO + HBr + C_6H_5OH,$$

but not a trace of the former substance, whose properties were carefully studied, could be found ; furthermore, it cannot have been formed as an intermediate product because special experiments with dibromacetaldehyde prove that it remains unchanged by treatment with the above named reagents.

Ten grams of phenyl dibromvinyl ether, 2 grams of water and 0.2 gram of phenol were heated in a sealed tube, for 4 hours, at 100°. On adding water, extracting with ether, washing with sodium carbonate, etc., 3.1 grams of bromacetic acid, b. p. 110° (22 mm.) and crystallizing on cooling, were obtained, theory = 4.1 grams. The part neutral to sodium carbonate was found to consist of 3 grams of phenol, b. p. 88° (22 mm.), theory = 3.3 grams. Eight grams of phenyl dibromvinyl ether and 20 cc. of absolute alcohol were heated in a sealed tube, at 100°, for 6.5 hours. Besides hydrogen bromide, 2.5 grams of phenol, b. p. 87° (25 mm.) and 4.8 grams of ethyl bromacetate, b. p. 156°, were obtained ; the latter gave, on treatment with aqueous ammonia, bromacetamide.

[1] Ann. Chem. (Liebig), 216, 282.
[2] *Loc. cit.*

Ten grams of phenyl dibromvinyl ether and 8 grams of glacial acetic acid were heated in a sealed tube, for 5 hours, at 100°. There were obtained 5.7 grams of phenyl bromacetate,[1] b. p. 140 (20 mm.), m. p. 32°.

0.2458 gram substance gave 0.2070 gram AgBr (Carius).

	Calculated for $C_8H_7O_2Br$.	Found.
Br	37.21	35.83

In conclusion, I wish to express my thanks and gratitude to Professor Nef for the inspiration and help which he has given me in this work.

Contributions from the Chemical Laboratory of the Nebraska Wesleyan University.

XI.—THE CONDENSATION OF THE THREE NITRANILINES WITH *p*-NITROSOBENZALDEHYDE.

By Frederick J. Alway and Ross A. Gortner.

Under favorable conditions many nitroso compounds react almost quantitatively with amino compounds to produce azo derivatives, according to the equation :

$$RNO + H_2NR' = RN : NR' + H_2O.$$

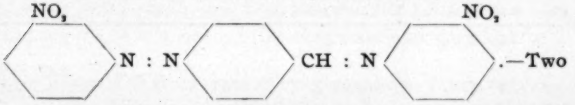
We have found that *p*-nitrosobenzaldehyde condenses readily with *m*-nitraniline, less readily with *p*-nitraniline and with so much difficulty with *o*-nitraniline that we were unable to isolate any of the condensation product.

The readiness with which the nitranilines condense with *p*-nitrosobenzaldehyde varies as their basicity. In regard to the latter property Kleemann[2] has shown that, when equal weights of the three hydrochlorides are boiled with the same volume of water for a short time, and then evaporated to dryness at 75°, there is decomposed into base and hydrochloric acid; of the

o-nitraniline hydrochloride		63.8 per cent
p- "	"	13.1 "
m- "	"	3.4 "

[1] Kunckell and Scheven : Ber. d. chem. Ges., 31, 172.
[2] Ibid., 19, 336 (1886).

m-Nitranilide of m-Nitrobenzene-p-azobenzaldehyde,



.—Two grams of *p*-nitrosobenzaldehyde, dissolved in 25 cc. of glacial acetic acid, were slowly added to a boiling acetic acid solution of 5 grams of *m*-nitraniline. The mixture became deep red in color and, after being kept near the boiling point for a few minutes, was allowed to cool slowly. Brick red, granular masses separated out. These were washed on the filter with 95 per cent alcohol and dried at 110°.

0.1756 gram substance gave 31.3 cc. moist N at 25° and 727 mm.

	Calculated for $C_{19}H_{13}O_4N_5$.	Found.
N	18.66	19.00

The compound melts at 239°.5 (corr.), is readily soluble in nitrobenzene but only sparingly soluble in ethyl alcohol, amyl alcohol and glacial acetic acid. It is only partly decomposed by cold, dilute nitric acid. By prolonged treatment with hot, dilute hydrochloric acid it is entirely resolved into *m*-nitrobenzene-*p*-azobenzaldehyde and *m*-nitraniline.

We obtained the same compound by the condensation of *m*-nitrobenzene-*p*-azobenzaldehyde with *m*-nitraniline, using glacial acetic acid as a solvent for both the reacting compounds.

m-Nitrobenzene-p-azobenzaldehyde, $O_2NC_6H_4N:NC_6H_4CHO$.—We have found that the substance to which this name was previously ascribed[1] consists largely of the condensation product described above, the decomposition of the latter by cold, dilute nitric acid having been incomplete.

The anilide, melting at 239°.5, was placed in a flask covered with dilute hydrochloric acid, 13 per cent, and kept at 60° to 80° for 1 hour. The resulting mixture was treated with cold

[1] THIS JOURNAL, 32, 398 (1904).

water and filtered. The residue was thoroughly washed with cold water, dried and recrystallized from dilute ethyl alcohol.

0.1849 gram substance gave 28.1 cc. moist N at 23° and 724 mm.

0.2348 gram substance gave 0.5241 gram CO_2 and 0.0173 gram H_2O.

	Calculated for $C_{13}H_9O_3N_3$.	Found.
C	61.2	60.9
H	3.5	3.4
N	16.5	16.3

This aldehyde forms minute, red needles melting at 135° (corr.). It is very soluble in ethyl alcohol, amyl alcohol, glacial acetic acid and nitrobenzene; fairly soluble in benzene, toluene, chloroform, ethyl acetate and acetone; and difficultly soluble in ether, methyl alcohol, ligroin and carbon bisulphide.

Phenylhydrazone of m-Nitrobenzene-p-azobenzaldehyde, $O_2NC_6H_4N : NC_6H_4CH : NNHC_6H_5$.—A solution of *m*-nitrobenzene-*p*-azobenzaldehyde in 95 per cent alcohol was treated with an excess of phenylhydrazine and heated on the water-bath for 1 hour. After the heating had been continued for some time crystals began to separate from the dark red solution. The crystals were washed on the filter with alcohol and dried at 100°.

0.1234 gram substance gave 23.6 cc. moist N at 25° and 724 mm.

	Calculated for $C_{19}H_{15}O_2N_5$.	Found.
N	20.3	20.3

This hydrazone forms dark red, rectangular plates, melting at 213°.5 (corr.).

Oxime of m-Nitrobenzene-p-azobenzaldehyde, $O_2NC_6H_4N : NC_6H_4CH : NOH$.—A solution of 0.7 gram of sodium hydroxide, in water, was treated with 0.4 gram of hydroxylamine hydrochloride, then with an alcoholic solution of 1 gram of *m*-nitrobenzene-*p*-azobenzaldehyde and finally heated for 1.5 hours on the water-bath. The red solution, so

obtained, was treated with water and acidified with acetic acid. The precipitate was filtered out, washed with water and recrystallized from dilute alcohol.

0.1817 gram substance gave 35.2 cc. moist N at 25° and 724 mm.

	Calculated for $C_{13}H_{10}O_2N_4$.	Found.
N	20.7	20.6

The oxime forms yellow crystals, melting at 116° (corr.).

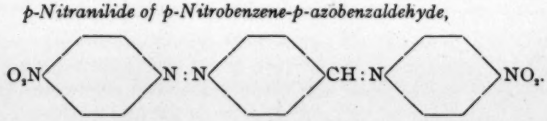
Anilide of m-Nitrobenzene-p-azobenzaldehyde, $O_2NC_6H_4N : NC_6H_4CH : NC_6H_5$.—A mixture of *m*-nitrobenzene-*p*-azobenzaldehyde with an excess of aniline was heated 1 hour at 110°, cooled and treated with absolute alcohol, which precipitated the anilide. The latter was filtered out, washed with alcohol, dried, dissolved in hot benzene and reprecipitated by the addition of absolute alcohol.

0.1383 gram substance gave 22.7 cc. moist N at 27° and 724 mm.

	Calculated for $C_{19}H_{14}O_2N_4$.	Found.
N	17.0	17.2

This compound forms small, yellow crystals, melting at 132° (corr.).

p-Nitranilide of p-Nitrobenzene-p-azobenzaldehyde,



—Six grams of *p*-nitrosobenzaldehyde, dissolved in hot, glacial acetic acid, were slowly added to a boiling solution of 15 grams of *p*-nitraniline in glacial acetic acid. The mixture was heated a few minutes and then allowed to cool slowly. A dark red, granular mass separated from the brownish-red solution on cooling. This was filtered out, washed on the filter with alcohol and recrystallized from glacial acetic acid. The crystals were washed on the filter with hot alcohol and dried.

0.2672 gram substance gave 44.5 cc. moist N at 20° and 734 mm.

	Calculated for $C_{19}H_{18}O_4N_6$.	Found.
N	18.7	18.4

This compound forms small, red needles, melting at 237°–238°.5 (corr.); it is sparingly soluble in alcohol but readily soluble in hot, glacial acetic acid.

p-Nitrobenzene p-azobenzaldehyde, $O_2NC_6H_4N:NC_6H_4CHO$.—The anilide, melting at 237°–238°.5, was treated with dilute hydrochloric acid, 3 parts of concentrated acid to 1 part of water. The mixture was kept at 60° for 2 hours and was then filtered, washed on the filter with hot, dilute hydrochloric acid and, finally, with alcohol. The crude product, so obtained, was recrystallized from glacial acetic acid.

I. 0.1348 gram substance gave 19.8 cc. moist N at 10° and 728 mm.

II. 0.2032 gram substance gave 0.4541 gram CO_2 and 0.0820 gram H_2O.

III. 0.1768 gram substance gave 0.3970 gram CO_2 and 0.0570 gram H_2O.

	Calculated for $C_{13}H_9O_3N_3$.	Found. I.	II.	III.
C	61.2	. .	60.9	61.3
H	3.5	. .	4.0	3.5
N	16.5	16.8	. .	. .

p-Nitrobenzene-*p*-azobenzaldehyde crystallizes in long, red plates, melting at 221°–222° (corr.). It is very soluble in hot benzene, glacial acetic acid, nitrobenzene and amyl alcohol, and moderately soluble in each of these solvents in the cold. It is fairly soluble in acetone, chloroform and ethyl acetate, and sparingly soluble in ethyl alcohol, methyl alcohol, ether, ligroin and carbon bisulphide.

Anilide of p-Nitrobenzene-p-azobenzaldehyde, $O_2NC_6H_4N:NC_6H_4CH:NC_6H_5$.—A mixture of *p*-nitrobenzene-*p*-azobenzaldehyde with an excess of aniline was heated to 110°, for 2 minutes and then cooled. The solid substance thus obtained was dried on a porous plate and recrystallized

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from benzene. In the preparation of this compound it is important that the heating be discontinued at the end of 2 minutes as, otherwise, the anilide seems to undergo decomposition.

0.1392 gram substance gave 21.3 cc. moist N at 20° and 724 mm.

	Calculated for $C_{19}H_{14}O_3N_4$.	Found.
N	17.0	16.7

This anilide forms stellate groups of orange-colored needles, melting at 152° (corr.) and is insoluble in absolute alcohol.

Oxime of p-Nitrobenzene-p-azobenzaldehyde, $O_2NC_6H_4N : NC_6H_4CH : NOH$.—A solution of 1 gram of sodium hydroxide in water was treated with 0.6 gram of hydroxylamine hydrochloride, then with an alcoholic solution of 1.5 grams of *p*-nitrobenzene-*p*-azobenzaldehyde and, lastly, was heated to boiling for 3 hours. The reaction product was treated with water and acetic acid and filtered. The residue was washed with alcohol and dried at 100°.

0.0986 gram substance gave 17.8 cc. moist N at 17° and 736 mm.

	Calculated for $C_{13}H_{10}O_3N_4$.	Found.
N	20.7	20.3

This oxime forms a yellow solid not melting below 290°.

We failed to obtain the phenylhydrazone of *p*-nitrobenzene-*p*-azobenzaldehyde in a pure condition.

Condensation of o-Nitraniline with p-Nitrosobenzaldehyde.—We tried to effect the condensation by the method that had succeeded in the case of *m*-nitraniline and *p*-nitraniline. The acetic acid solution became red, indicating the formation of some azo compound. However, even after 3 hours' heating, at the boiling point of acetic acid, with an excess of *o*-nitraniline, a large amount of unchanged *p*-nitrosobenzaldehyde remained, as we were able to demonstrate by distillation with steam. From the small amount of residue after the treatment with steam we were unable to isolate any condensation product.

UNIVERSITY PLACE, NEBRASKA,
June 15, 1906.

VARIABLE SENSITIVENESS IN COLORIMETRY. III.

By David W. Horn and Sue A. Blake.

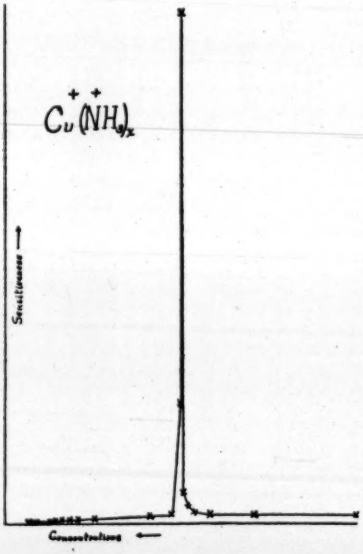
In extending the investigation of the relation between sensitiveness and concentration in colorimetry, we have studied ammoniacal solutions of copper sulphate. The results of this study and a graph based upon them are given below. The same phenomena are to be observed here as in the cases previously described. A constant fraction and a constant ratio characterize our measurements in these solutions as they did in solutions of copper sulphate in water. The remarkable increase and the subsequent rapid decrease in sensitiveness that occur near the maximum of sensitiveness have been studied more closely in this case than heretofore, with the result that the maximum of sensitiveness appears to be even more accentuated than we have previously indicated.

The experimental results follow:

Table I.—Ammoniacal Solutions of Copper Sulphate.

Number of experiment.	Concentration stated as liters that contain one gram atom of Cu.	Milligrams of Cu producing a just perceptible difference in color in 50 cc.	Sensitiveness: reciprocals of values found in column 3.	$\frac{\sqrt{V}}{14}$.	$\frac{S}{85}$.
1.	2.	3.	4.	5.	6.
1	83.6	1.905	0.52	0.65	0.006
2	100.0	2.220	0.45	0.71	0.005
3	125.2	1.651	0.61	0.80	0.007
4	166.8	1.016	0.98	0.92	0.012
5	277.7	0.7314	1.37	1.19	0.016
6	333.3	0.5724	1.75	1.31	0.020
7	384.6	0.4452	2.25	1.40	0.026
8	500.0	0.3180	3.14	1.60	0.037
9	666.6	0.2385	4.19	1.83	0.049
10	799.9	0.1987	5.03	2.02	0.059
11	1250.0	0.1272	7.86	2.53	0.092
12	3333.3	0.0636	15.72	4.13	0.185
13	4443.9	0.0530	18.87	4.76	0.222
14	4966.9	0.0034	294.12	5.03	3.46
15	4996.1	0.0008	1250.00	5.04	14.71
16	5000.0	0.0132	75.75	5.05	0.89
17	5332.7	0.0265	37.87	5.21	0.44
18	5714.3	0.0397	25.25	5.40	0.29
19	6666.6	0.0795	18.94	5.83	0.22
20	10000.0	0.0795	18.94	7.14	0.22
21	20000.0	0.0795	18.94	10.10	0.22

The results in Table I., when plotted, give the following graph, in which the ordinates are proportional to the square roots of the sensitiveness and the abscissae to the concentrations:



The results in Table I. are amplified in Table II. to show:

1. The ratio between the amount of copper that just suffices to produce an appreciable difference in color in 50 cc. of each solution and the total amount of copper present in 50 cc. of the solution at the different concentrations studied. This ratio is represented in the table by Δ/β'. This value Δ/β' multiplied by 100, gives directly the percentage error inherent in the comparisons of the color.

2. The ratio between the total amounts of copper in two 50 cc. tubes containing solutions that exhibit the minimum perceptible difference in color. This ratio is represented in the table by β/β'.

In Table II. the experiments are numbered and given in the same order as in Table I. :

Table II.—Ammoniacal Solutions of Copper Sulphate.

Number of experiment.	Milligrams Cu: β.	Milligrams Cu producing just perceptible color in 50 cc. Δ.	$\beta' = \beta + \Delta$.	Δ/β'.	Variation from mean in experiments 1–13, inclusive.	β/β'.	Variation from mean in experiments 1–13, inclusive.
1.	2.	3.	4.	5.	6.	7.	8.
1	38.100	1.905	40.005	0.05	−0.006	0.95	+0.005
2	31.750	2.220	33.970	0.07	+0.014	0.94	−0.005
3	25.400	1.651	27.051	0.06	+0.004	0.94	−0.005
4	19.050	1.016	20.066	0.05	−0.006	0.95	+0.005
5	11.448	0.7314	12.1794	0.06	+0.004	0.94	−0.005
6	9.540	0.5724	10.1124	0.06	+0.004	0.94	−0.005
7	8.268	0.4452	8.7132	0.05	−0.006	0.95	+0.005
8	6.360	0.3180	6.6780	0.05	−0.006	0.95	+0.005
9	4.770	0.2385	5.0085	0.05	−0.006	0.95	+0.005
10	3.975	0.1987	4.1737	0.05	−0.006	0.95	+0.005
11	2.544	0.1272	2.6712	0.05	−0.006	0.95	+0.005
12	0.954	0.0636	1.0176	0.06	+0.004	0.94	−0.005
13	0.716	0.0530	0.7690	0.07	+0.104	0.93	−0.015
14	0.640	0.0034	0.6434	0.005			
15	0.637	0.0008	0.6378	0.001			
16	0.636	0.0132	0.6492	0.02			
17	0.596	0.0265	0.6225	0.04			
18	0.556	0.0397	0.5957	0.07			
19	0.477	0.0795	0.5565	0.14			
20	0.318	0.0795	0.3975	0.20			
21	0.159	0.0795	0.2385	0.33			

One of the most interesting points that appears when these tables are compared with those in the preceding paper is the close agreement in the values for the ratio β/β' for the copper-blue and the cuprammonium-purple. In the one case the average value is 0.92 and in the other 0.94. There is a sug-

gestion in this of the possibility that the ratio β/β' is a constant that is independent of the color examined. This can be tested by the study of the compounds of the same element that have different colors in solution. Data involving different elements are at present not comparable, for the term "gram-atomic color" has no significance that is known, nor is any idea analogous to the one it would express generally accepted.

The concordance in the data obtained up to the present in this investigation, considered along with the satisfactory character of the interpretation of these data in terms of "the *fundamental* psycho-physical law"—Weber's Law—make it very probable that the following generalizations apply to colorimetric analysis as a whole :

Equal weights of colored solute do not produce equal differences in color *except* when they are added to colored solutions whose concentrations are equal. For example, only 0.00027 as much potassium chromate must be added to a 0.000125 N solution of chromate to change its color perceptibly as must be added to a 0.004 N solution to produce a perceptible effect; and about 13 times as much chromate must be added to distilled water to give the water a visible color as must be added to a 0.000125 N solution of chromate to change its color perceptibly.

The weight of colored solute required to produce a just perceptible difference in color when added to a colored solution varies greatly with the concentration of the colored solution, and varies in a very irregular way, but the general behavior is the same in all cases and is independent of the color under examination. This may be seen in the forms of the graphs for $\overset{--}{CrO_4}$, $\overset{++}{Cu}$ and $Cu(\overset{++}{N}H_3)_x$.

The whole range of concentrations from those of solutions too deeply colored for use, to those of solutions too feebly colored to be distinguishable from distilled water exhibits 3 different and characteristic sets of relations between sensitiveness and concentration. For clearness, these 3 parts of the total range will be dealt with separately.

The first begins with the most concentrated solutions that

can be used in colorimetry and includes a large number of lesser concentrations, at any one of which the relation between sensitiveness and concentration is expressed by the law that *the sensitiveness varies inversely as the concentration*, or, *the product of the sensitiveness into the total weight of colored solute present is a constant*. This law may be stated in other forms so that the sensitiveness—a term defined arbitrarily in the first paper of this series—does not enter into consideration. Thus, *the weight of colored solute that must be added to a colored solution to produce a just perceptible difference in color is a constant fraction of the total weight of colored solute present*; in this form there is an example of the law to be found in column 5, Table II. Another statement is that *the weights of colored solute in any 2 solutions that are just distinguishable by color bear a constant ratio to each other*, and an example of the law in this form may be found in column 7, Table II. It has been shown in the preceding paper that throughout the range in which the above law is valid, the percentage error arising from the limitation of the eye in the matching of colors is constant and independent of the concentrations of the solutions compared.

The second begins where the above law ceases to be valid. From this point on the weight of colored solute required to produce a perceptible difference in color becomes rapidly a smaller and smaller fraction of the total weight of colored solute present, attains and passes through a minimum limiting value, and then rapidly becomes a larger and larger fraction of the total weight of colored solute present. For example, in ammoniacal solutions of copper sulphate the fraction within the first part of the range of concentrations has a constant value of about 0.055, whereas in the second it rapidly reaches a value of 0.001 and then rises suddenly to a value of 0.02. At the concentration corresponding to the minimum value of the fraction the percentage error in the estimation of color will have but about 0.018, the value that it had in the first part of the range. It is within this *second* part that all colorimetric analyses should be made. The nearer the concentrations of the solutions in the analyses are to those corresponding to the minimum value of the fraction, *i. e.*, to the maximum sensi-

tiveness, the less the necessary percentage error due to the eye in the estimation of the colors.

The third range may be considered as commencing where the fraction just mentioned acquires a value greater than it had in the first. This third part includes solutions that are very faintly colored. The eye is unable, finally, to distinguish the solutions from distilled water. Usually the percentage error is considerably greater in this third range than elsewhere, so that solutions having these concentrations should be avoided in colorimetric analysis.

It seems to us that data such as we have represented by the curve of sensitiveness must be known in each colorimetric method if the method is to be used to greatest advantage and the results are not to be affected by errors of unknown magnitudes. When such data have been accumulated for the several important methods it will be possible, by a comparison of these data, to establish the relative merits of different colorimetric methods that have been suggested for the same purposes. In the absence of these data, colorimetric analysis lacks an exact and satisfactory basis.

CHEMICAL LABORATORY,
BRYN MAWR COLLEGE,
June, 1906.

OBITUARY.

WILHELM MEYERHOFFER.

Professor Wilhelm Meyerhoffer was born at Pinsk, Russia, September 13, 1864, and died April 21, 1906. His education was obtained at Czernowitz, Heidelberg and Strassburg. He received the Ph.D. from the University of Amsterdam, in 1889, his research, an investigation of cupribipotassium chloride, being carried out under the direction of Professor van 't Hoff. After brief residences in Vienna, Paris and Leipzig he returned to van 't Hoff, with whom he has ever since been closely associated. In addition to his title of professor, he has been for many years a "Privatdozent" of the University of Berlin.

Meyerhoffer is best known for his investigations of heterogeneous equilibria and his work, with van 't Hoff, on the formation of the Stassfurt salt beds. In 1892 he published a text-book on Stereochemistry, followed, in 1893, by an ad-

mirable volume on the "phase rule;" he was also chiefly responsible for the publication of the last (5th) edition of Landolt-Börnstein's "Physikalisch-Chemische Tabellen," in 1905.

REVIEWS.

PETROGENESIS. Von C. DOELTER, o. Professor der Mineralogie und Petrographie an der Universität Gratz. Die Wissenschaft. Sammlung naturwiss. u. math. Monographien. Heft 13. Braunschweig: Vieweg und Sohn. 1906. Price, M. 7, geb. M. 7.80.

This little volume, forming the thirteenth monograph in the series issued by F. Vieweg and Son, maintains the high standard of excellence shown by previous issues. It is a timely resumé of the large amount of work which has appeared in recent years on the Origin of Rocks. The present book is based more largely on experimental work on the formation of minerals and rocks than has been the case heretofore. The 14 chapters, with the brief subject and author indices, permit one to gain ready access to the latest views regarding the mode of origin of the different kinds of rock constituting the earth's crust.

The first half of the discussion is devoted to igneous rocks and includes a digest of the modern investigations regarding vulcanism and the interior of the earth, the external features and structure of eruptive rocks, the chemical peculiarities of rocks and the causes producing them, and the artificial production of known rocks. The latter half is given to a consideration of the metamorphic and sedimentary rocks and to chemical precipitates.

The discussions in each case are timely and well proportioned, and give the views of the various investigators. It is a matter of regret, however, that these views have not been more thoroughly digested and the results generalized in summary paragraphs. The treatment throughout is from the chemico-physical standpoint, rather than the geological. The book is not a text-book of petrography, but an attempt to bring together such facts and theories as may aid in explaining why rocks are as we find them. The style is clear and the statements concise, but the demand on the knowledge of the reader is great. There is, however, no other book which so clearly outlines the attempts which are now being made to apply physico-chemical laws to the complex problems presented by the reactions taking place in the solid crust of the earth.

E. B. M.

LES NOUVEAUTÉS CHIMIQUES POUR 1906. Nouveaux Appareils de Laboratoire, Méthodes nouvelles de Recherches Appliquées a la Science et a l'Industrie, par CAMILLE POULENC, Docteur ès Sciences. Avec 203 Figures intercalées dans le Texte. Paris: J. B. Baillière et Fils. Price, 4 Fr.

This new number of Dr. Poulenc's excellent yearbook includes practically all of the improvements in apparatus made within the last 12 months in France and in Germany. Although the novelties this year are less important than last, the book is worth perusal, as it contains descriptions of many minor improvements. E. R.

THEORIEN DER CHEMIE. Nach Vorlesungen gehalten an der Universität von Kalifornien zu Berkeley. Von SVANTE ARRHENIUS. Mit Unterstützung des Verfassers aus dem englischen Manuskript. Übersetzt von ALEXIS FINKELSTEIN. Leipzig: Akademische Verlagsgesellschaft m. b. H. 1906. pp. 177.

As the title implies, this is the German translation of Arrhenius' lectures at the University of California, during the summer of 1904. In this case, as in most others, the best idea of the ground covered can be gained by a glance at the "contents."

The several chapters deal with "The Uses of Theories; Older Theories in Chemistry—Dalton's law; Discussion of the Validity of the Laws of Dalton; Electrical Forces between Atoms—Faraday's Law; Electrical Forces between Atoms—Chemical Valence and Affinity; The Development of the Conception of Valence; Composition of the Atoms—Electrons; Theory of Gases; Chemical Kinetics and Statics; The Effect of Temperature and Pressure—Dissociation; Osmotic Pressure, General Laws of Dissolved Substances; Electrolytic Dissociation; Unsolved Problems.

It is needless to add that the discussion of these matters is thoroughly up to date, and shows the hand of the master at every turn. This is, of course, just what would be expected from one of the founders of the new school of physical chemistry. As is so well known, it was Arrhenius who, to account for the i in the van't Hoff equation for osmotic pressure, $PV = iRT$, gave the world the theory of electrolytic dissociation—one of the four great generalizations upon which modern physical chemistry rests. The book is comparatively elementary, and should be read by all who are interested in the theories upon which scientific chemistry is based. H. C. J.

DIE CHEMISCHE REICHSANSTALT. Von WILHELM OSTWALD. Leipzig: Akademische Verlagsgesellschaft m. b. H. 1906. pp. 28.

This little pamphlet by Ostwald is of unusual interest, not only on account of the vivid and fascinating style in which it

is written, but because of the number of important problems which it discusses.

On the 21st of February about 150 persons, interested in scientific and technical chemistry, met in the "Aula" of the University of Berlin to discuss the feasibility of founding a chemical "Reichsanstalt."

In addition to the special problem under consideration, Ostwald discusses in this pamphlet a number of general relations that are of the very highest importance for the development of scientific chemistry. In reference to the possibility of good work being done under unfavorable conditions, says Ostwald, "Es ist ja wahr dass viele grosse Entdeckungen mit sehr bescheidenden Mitteln gemacht worden sind, und dass das Genie eines grossen Mannes glorreich überwinden kann. Aber daneben bleibt doch dass Gesetz von der Erhaltung der Energie unerschüttert stehen, und dieses besagt in dem vorliegenden Falle, dass jene grossen Männer noch mehr geleistet hätten, wenn wir den Teil ihrer Energie, den sie zur Überwindung der äusseren Hindernisse zu verbrauchen hätten, unmittelbar auf rein wissenschaftliche Arbeit hätten anwenden dürfen. Die schönen Apparate und Arbeitsräume tun es freilich nicht allein, Sie sind nur ein Faktor in dem Produkt, und das Produkt bleibt Null, wenn der andere Faktor, die Intelligenz des Forschers Null ist. Aber anderenseits wächst das Produkt proportional dem Betrag jedes einzelnen Faktors."

Apparently the most prominent figures in this new movement are Professors Emil Fischer and Walter Nernst. The field in which such an institution as that now under consideration is most needed is in analytical chemistry. This institution should make provision for at least the following lines of work: Inorganic chemistry, especially the determination of atomic weights. There should be equipment also for general analytical chemistry, for organic chemistry, and for physical chemistry.

Ostwald pays high tribute to the work of Richards on atomic weights, but this field requires the co-operation of a number of permanent workers. Then the scientific side of metallurgy calls urgently for investigators.

In organic chemistry there is great need of further development in certain directions, especially in the technical applications of organic substances.

In physical chemistry the needs are most pressing. "Diese hat zunächst die wichtigsten Konstanten der reinen Stoffen neu und einheitlich zu bestimmen, d. h. etwa den ganzen Landolt-

Börnstein experimentell neu zu bearbeiten." In addition, the dissociation constants of acids and bases, the solubility of salts, the dielectric constants of organic compounds, should be redetermined. Further, the dynamics of typical reactions, thermochemistry, and especially *catalysis* should be thoroughly investigated. "Die Grundlagen stehen ja fest; eine Unzahl qualitativer Vorgänge im Gebiete der Katalyse sind bekannt, sie brauchen nur systematisch-quantitativ durchgearbeitet zu werden."

The following statement will be of special interest to all Americans: "In der Tat, wenn es ausserhalb Deutschlands ein Land gibt, in welchem die praktische Bedeutung der Wissenschaft klar erkannt wird, so sind es die Vereinigten Staaten."

After discussing the condition of technical affairs, especially in England, Ostwald closes with the significant words: "Darum muss unsere erste und wichtigste Sorge sein, den Plan so schnell als möglich auszuführen. Denn darüber darf man nicht im Zweifel sein; ist eine solche Anstalt einmal vorhanden, so wirkt sie nicht nur katalytisch, sondern auch autokatalytisch, und darum ist für uns Gefahr im Verzuge." H. C. J.

JAHRBUCH DER ELEKTROCHEMIE UND ANGEWANDTEN PHYSIKALISCHEN CHEMIE. Begründet und bis 1901 herausgegeben von PROF. DR. W. NERNST and PROF. DR. W. BORCHERS.

BERICHTE ÜBER DIE FORTSCHRITTE DES JAHRES 1904. Herausgegeben von DR. PHIL. HEINRICH DANNEEL. XI. Jahrgang. Breslau. Halle a. S.: Verlag von Wilhelm Knapp. 1906. pp. 937. Price, M. 28.

The "Jahrbuch der Elektrochemie" for 1904 differs from the earlier volumes in being, if possible, even more thorough and complete. Rather more space is given to scientific electrochemistry than to applied, the first 556 pages being devoted to the former.

This is easily the most thorough and useful "Jahrbuch" with which the present writer is familiar. The reviews of the various papers are elaborate enough to give a satisfactory conception of their contents, which is more than can be said of many so-called reviews of scientific articles.

One is deeply impressed by the amount of labor that must be expended annually in preparing such a work. It is fair to say that an undertaking of this nature could be carried out successfully only in one country in the world, and that country is Germany.

This "Jahrbuch" will prove of incalculable value to all active workers in the field of electrochemistry, and will be of special use to those who do not have ready access to the original arti-

cles. It will, doubtless, find its way into every scientific library and into every laboratory where scientific work is being done. It is one of the few books upon which only the highest praise can be bestowed. H. C. J.

LABORATORY MANUAL OF GENERAL CHEMISTRY (Fourth Edition). By THOMAS EVANS and J. F. SNELL. Cincinnati: University Press, University of Cincinnati, Ohio. 1905. pp. 70. Price, $0.50.

This manual has been written to meet the special needs of students at the University of Cincinnati. The experiments are, in the main, those found in most text-books for students just beginning the study of chemistry; but, as the authors state in the preface, in addition to these certain special experiments have been selected from various books. The choice is good and in most cases the experiments are clearly described, but, of course, such a manual can only be used to advantage in connection with a text-book in which the theory can be followed step by step. The reviewer has found that satisfactory results in quantitative experiments can only be obtained by the beginner under the constant personal supervision of the instructor, and he does not believe that the number of such experiments given in the early part of this book could be followed with advantage to the student except with small classes, or with a greater number of assistants than are usually found in such laboratories. If the chemical course follows a course in physics, where precision and care have been taught, this method might be used; but the first-year chemical courses in colleges are usually taken by those who have had so little training in scientific methods that they do not have the proper conception of the requirements of such work and not enough knowledge of the principles involved to successfully carry out the directions. J. E. G.

ANLEITUNG ZUM GEBRAUCH DES POLARISATIONSMIKROSKOPS. Von DR. ERNST WEINSCHENK. Freiburg i/B.: Herdersche Verlagshandlung. 1906. Price, $1.25 net.

This is the second edition of a most useful laboratory book, the first edition of which appeared in 1901. There is no one who can speak with greater authority in regard to the questions pertaining to petrography, or who is better known as a teacher than the author. The present volume contains 147 pages and is enriched with 135 figures and illustrations. The work begins with a discussion of the microscope and its adjustments for use with polarized light. This is followed by chapters on observations with ordinary light, with a parallel beam of polarized light, and with convergent polarized light. After this come the chapter in regard to twinning crystals and

various optical phenomena and an appendix describing in detail various pieces of apparatus.

The work is admirable in every respect and is to be recommended to every student of mineralogy and to those students of physics who are interested in the phenomena of polarized light.

J. S. A.

DIE ELEKTROLYSE GESCHMOLZENER SALZE. Dritter Teil, Elektromotorische Kräfte. Von RICHARD LORENZ, Dr. phil. o. Professor für elektrochemie und physikalische Chemie am eidg-Polytechnikum in Zurich (Monographien über angewandte Elektrochemie). Mit 75 in den Text gedruckten Abbildungen. Halle a. S.: Druck und verlag von Wilhelm Knapp. pp. 322. 1906. Price, M. 10.

The earlier parts of this monograph on the electrolysis of fused salts have already been noticed earlier.[1] The third part, as the title implies, deals with electromotive force. The subject is treated under the five general headings: Polarization, Elements, Electromotive Force and Chemical Heat (Free Energy), Decomposition Tension and the Ionic Theory.

This portion of the monograph seems to have been worked up with the same thoroughness as those that preceded it.

H. C. J.

GRUNDRISS EINER ENTWICKELUNGSGESCHICHTE DER CHEMISCHEN ATOMISTIK, zugleich Einführung in das Studium der Geschichte der Chemie. By DR. RICHARD EHRENFELD, Privatdozenten an der k. k. technischen Hochschule in Brünn. Heidelberg: Carl Winter's Universitätsbuchhandlung. 1906. pp. viii + 314.

The author has sought to bring together, in systematic form and historical sequence, the various steps in the development of the conceptions of the constitution of matter which led to the formulation of Dalton's atomic hypothesis. He has included the purely speculative notions as well as the hypotheses which have been the outcome of experimentation and begins with such early Greek conceptions of the constitution of matter as those of Anaxagoras, Empedocles, Democrities and Epicunies. This is followed by a discussion of the period dominated by the Aristotelian philosophy and the relation of this period to that of alchemy, in which it is shown that the notions of the transformation of the simple elements, earth, air, fire and water, the one into the other, suggested the possibility of the transmutation of the metals. Alchemy, with its first faint suggestions of chemical science, is discussed at length, and also the spread of alchemy from Arabia into Christian lands. The teachings of Paracelsus, Van Helmont and others of their contemporaries lead up to the corpuscular theory of Robert Boyle, and this, in time, to the phlogistic

[1] THIS JOURNAL, 33, 373, 547 (1906).

theory and the first conceptions of a chemical compound. All of this is considered in its bearings upon the theory of Dalton, which is fully discussed, from the point of view of its limitations, as well as its usefulness. The author then considers, at length, some of the views more recently expressed regarding the probable complexity of the atoms as conceived by Dalton, especially those of Thomson and of Rutherford and Soddy, based upon the study of the radio-active elements. In conclusion, he presents, in outline, the position of Wald and that of Ostwald, who deduce the fundamental principles, such as the laws of constant and multiple proportions, without recourse to any conception of the existence of a chemical atom, such as the hypotheses of Dalton presupposes.

The book should be of interest to students of the history of chemistry, as the author takes pains to point out the influence exerted by each school of philosophers and thinkers upon those succeeding them, and to demonstrate the dependence of the teaching of each school upon some of the earliest of the philosophers. The work is of a specialized character, as indicated by the outline above, and would not serve as a general text-book of the history of the science. H. P. TALBOT.